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Utilization of Papermill Sludges as Binders for Iron Ore Concentrate

By Larry A. Haas, Jeffrey A. Aldinger, and John C. Nigro

BUREAU OF MINES

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Btu/lb	British thermal unit per pound	lb/p	pound per pellet
Btu/st	British thermal unit per short ton	m	meter
cm	centimeter	μm	micrometer
cm^3/g	cubic centimeter per gram	mL	milliliter
°C	degree Celsius	mm	millimeter
°C/h	degree Celsius per hour	mm Hg	millimeter of mercury (atmospheric pressure)
°C/min	degree Celsius per minute	min	minute
ft	foot	pct	percent
g	gram	pct/min	percent per minute
g/cm^3	gram per cubic centimeter	ppb	part per billion
g/mL	gram per milliliter	ppm	part per million
h	hour	psig	pound per square inch, gauge
in	inch	rpm	revolution per minute
kg	kilogram	SLM	standard liter per minute
kg/cm^2	kilogram per square centimeter	st	short ton
L	liter	st/d	short ton per day
lb	pound	wt pct	weight percent
lb/d	pound per day	yd^3/yr	cubic yard per year

UTILIZATION OF PAPERMILL SLUDGES AS BINDERS FOR IRON ORE CONCENTRATE

By Larry A. Haas,[1] Jeffrey A. Aldinger,[2] and John C. Nigro[3]

ABSTRACT

The U.S. Bureau of Mines, in cooperation with the Iron Range Resources and Rehabilitation Board, investigated the potential of using northeastern Minnesota papermill waste sludges as a binder for Mesabi Range iron ore (taconite) concentrate. Sludges from five different commercial papermill waste treatment operations were evaluated in laboratory tests. Except for the coarsest sludge, all were fairly easy to blend with the taconite concentrate using conventional mixing methods. The coarsest sludge had to be reslurried at 2 pct solids before adding it to the concentrate in order to obtain pellets without visible sludge clumps. Drying and grinding the sludges made them less effective as binders because of a lower degree of rehydration.

On a dry weight equivalent basis, twice as much raw sludge binder was required to obtain similar pellet physical properties as with bentonite; however, the pellets made with raw sludge had superior metallurgical properties. Over 30 pct higher reduction rates and over 150° C higher softening temperatures were obtained with sludge binder than with bentonite. Sludge D, which had the lowest fiber and the highest alkali metal content, resulted in the lowest reducibility enhancement. Even though more raw sludge was required than bentonite, the sludges have virtually no value, and therefore may provide a cost-effective additive binder for producing improved metallurgical-quality pellets. Large-scale testing has not been done to confirm these laboratory results.

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INTRODUCTION

The Bureau is investigating different technology options for producing improved domestic iron oxide pellets. Historically, about 70 pct of domestic iron ore pellets have been produced in northern Minnesota's Mesabi Range, but production decreased during the early 1980's (*1-2*).[4]

The international iron ore pellet market has eroded the competitiveness of domestic iron ore producers. Some foreign producers have several advantages over the domestic producers, including direct and indirect national subsidies, favorable tax systems, lower labor costs, and guaranteed low transportation costs. Domestic producers are faced with more expensive environmental and safety regulations than other producers, especially those in lesser developed countries. Domestic producers are also mining lower grade deposits than their foreign competitors. To restore its competitiveness, the U.S. iron ore industry must apply innovative and less expensive methods for converting its low-grade iron ore into superior quality pellets.

Mesabi Range iron ore concentrates are extremely fine and must be pelletized (with a binder) before they can be used as blast furnace feed material. Approximately 15 pct of the total pellet cost is attributed to pelletizing. Bentonite, the conventional binder, is mined mainly in Wyoming and transported to pelletizing operations in the Lake Superior region. Approximately two-thirds of the total binder cost is attributed to shipping expenses. A sizable savings could be realized if a suitable binder could be obtained from sources closer to the pelletizing plants.

In the past, many pure organic binders have been investigated as substitutes for bentonite (*3-18*), but very little research has been conducted with inexpensive organic processing waste products. Some research (*19*) has been done with peat moss, which has some properties similar to waste pulpmill and papermill sludge, but contains more ash. Two reasons why organic binders have not been widely adopted are (1) their high cost and (2) the lack of adequate data on binder effectiveness (*5*). Adequate binder evaluation methods are presently not available for predicting the effectiveness of organic binders (*20*). Therefore the goals of this research were to (1) interrelate the binder characteristics with the pellet properties and (2) compare the physical and metallurgical properties of pellets made with paper sludge and bentonite binders. For simplicity, the pulpmill and papermill sludges are referred to in this report as paper sludges. Considerable research (*21-28*) has been done on disposal and uses for paper sludge, but essentially no literature is available on its effectiveness for agglomerating taconite concentrate. A discussion of some sludge uses and the properties that must be considered to evaluate its overall potential as a binder is given in the appendix.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to the Iron Range Resources and Rehabilitation Board, Mines and Reclamation Division, Calumet, MN, for partially funding this research.

MATERIALS

The binder materials consisted of a typical commercial bentonite (BEN17) clay (*29*), paper sludges, and some of the pure materials found in paper sludges. Each binder used in this study was given an alphanumeric code to shorten the reference to that binder in the text, graphs, and tables (table 1). Physical characteristics of the binder materials are given in table 2. The pure materials are kaolin clay and pure organic polymers, which were included in this study to better understand the binder effectiveness of paper sludges. The polymers were nongelled starch (SC71), pregelled starch (SWG70), pregelled guar gum (GG211), and pregelled carboxyl methyl cellulose (CMCH1). The polymers and clays were received in powder form and were dried at 75° C overnight before they were chemically analyzed (table 3).

The waste sludges were obtained from five different sludge treatment operations (designated as B, C, D, R, and S) and consisted mainly of primary and/or secondary settler sludges and their mixtures (table 1). Sludges from two operations also contained municipal sewage waste. From three of the sources, two or more samples were obtained at approximately yearly intervals. A biocide of 1 pct Dowcil 75[5] or formaldehyde was added to some of the raw sludge samples to retard biodegradation of the sludge. The sludges that did not contain a biocide were refrigerated.

A Mesabi Range taconite concentrate was used as a wet filter cake or as a dry powder. The chemical analyses of the concentrate, dried overnight at 105° C, is also given in table 3. The dry concentrate density was 4.9 g/cm^3, and 70 pct of the particles were finer than 500 mesh.

[4]Italic numbers in parentheses refer to items in the list of references preceding the appendix at the end of this report.

[5]Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

Table 1.–Explanation of binder codes

Code	*Description*
Clays:	
BEN17	Bentonite 17.
KAOL1	Kaolin 1.
Pure organic polymers:	
CMCH1	Pregelled carboxyl methyl cellulose H1.
GG211	Pregelled guar gum 211.
SWG70	Pregelled wheat starch 70.
SC71	Nongelled corn starch 71.
Sludges:	
WmDs1	Waste sludge D, municipal sewage and secondary papermill settler sludge, 1st sample.
WmDs1b	WmDs1 with biocide added.
WmDs1-5	WmDs1 dried at ambient conditions for 5 days.
WmDs1d	WmDs1 dried overnight at 75° C and ground to minus 100 mesh.
WmDs2	Same as WmDs1, only 2d sample.
WmDs2d	WmDs2 dried overnight at 75° C and ground to minus 100 mesh.
WmpRs1	Waste sludge R, municipal sewage and primary and secondary papermill settler sludge, 1st sample.
WmpRs1d	WmpRs1 dried overnight at 75° C and ground to minus 100 mesh.
WmpRs2	Same as WmpRs1, only 2d sample.
WmpRs2b	WmpRs2 with biocide added.
WmpRs3	Same as WmpRs1, only 3d sample.
WmpRs3b	WmpRs3 with biocide added.
WmpRs3bd	WmpRs3b dried overnight at 75° C and ground to minus 100 mesh.
WmpRs3bP	WmpRs3b partially dried from 77 to 33 pct H_2O.
WmpRs3bPt	WmpRs3bP torn up by rubbing through a 4-mesh screen.
WmpRs3bP1S	The 1-h sediment of WmpRs3bP dispersed in water at 2 pct solids.
WmpRs3bP7S	Same as WmpRs3bP1S, only 7-h sediment.
WmpRs3bP7L	Same as WmpRs3bP7S, only 7-h suspension.
WmpRs3br	WmpRs3b wet rod mill ground for 30 min at 2 pct solids.
WmpRs3b/B	WmpRs3b with 30 pct dry equivalent BEN17 added.
WmpRs3d	WmpRs3 dried overnight at 75° C and ground to minus 100 mesh.
WpBs1	Waste sludge B, primary and secondary papermill settler sludge, 1st sample.
WpBs1-	Minus 400-mesh fraction of WpBs1.
WpBs1+	Plus 400-mesh fraction of WpBs1.
WpBs1d	WpBs1 dried overnight at 75° C and ground to minus 100 mesh.
WpBs2	Same as WpBs1, only 2d sample.
WpBs2d	WpBs2 dried overnight at 75° C and ground to minus 100 mesh.
WpC1	Waste sludge C, primary papermill settler sludge, 1st sample.
WpC1d	WpC1 dried overnight at 75° C and ground to minus 100 mesh.
WpC1r	WpC1 wet rod mill ground for 30 min at 2 pct solids.
WpR2	Waste sludge R, primary papermill settler sludge, 2d sample.
WpR3b	Same as WpR2, only 3d sample with biocide added.
WpS1	Waste sludge S, primary papermill settler sludge, 1st sample.
WpS1b	WpS1 with biocide added.
WpS1d	WpS1 dried overnight at 75° C and ground to minus 100 mesh.
WpSs1	Waste sludge S, primary and secondary papermill settler sludge, 1st sample.
WpSs1-5	WpSs1 dried at ambient conditions for 5 days.
WpSs1b	WpSs1 with biocide added.

Table 2.–Physical characteristics of clays, pure organic polymers, and sludges

Binder[1]	Wet properties				PWAT,[2] pct	Briquet dry shrinkage,[6] pct	Ash properties[3]	
	Texture	Density,[4] g/mL	Water,[5] pct	Plasticity			Color	Consistency
Clays:								
BEN17	Fine	1.04	[7]67	Soft	940	71	NE	NE.
KAOL1	do	.36	[7]36	do	50	20	NE	NE.
Polymers:								
CMCH1	do	.68	[7]73	do	3,260	81	NE	NE.
GG211	do	.71	[7]85	do	1,030	81	NE	NE.
SWG70	do	.61	[7]70	do	760	68	NE	NE.
SC71	do	.63	[7]53	do	110	49	NE	NE.
Sludges:								
WmDs1	do	1.04	82	do	[8]60	[9]78	NE	NE.
WmDs1d	do	NE	[7]43	do	130	43	NE	NE.
WmDs2	do	.97	82	do	[8]<30	[9]87	Brown	Brittle.
WmDs2d	do	NE	[7]43	do	100	47	NE	NE.
WmpRs1	Coarse	NE	76	Firm	NE	NE	NE	NE.
WmpRs2	do	.93	78	do	NE	NE	NE	NE.
WmpRs3b	do	.99	77	do	[8]60	NE	Tan	Soft.
WmpRs3bd	Fine	NE	[7]68	Soft	400	32	NE	NE.
WmpRs3bP	Coarse	.72	33	Firm	[8]110	NE	NE	NE.
WpC1	do	.92	62	do	[8]80	NE	Tan	Soft.
WpC1d	Fine	NE	[7]57	Soft	180	22	NE	NE.
WpR3b	Coarse	.84	73	Firm	[8]90	NE	Tan	Soft.
WpS1	do	.96	65	do	[8]110	NE	Tan	Do.
WpS1d	Fine	NE	[7]59	Soft	50	27	NE	NE.
WpBs1	do	NE	58	do	NE	NE	Rusty.	Hard.
WpBs1d	do	NE	NE	do	70	NE	NE	NE.
WpBs2	do	1.11	59	do	[8]<30	NE	Rusty.	Hard.
WpBs2d	do	NE	[7]40	do	80	33	NE	NE.
WpSs1	Coarse	1.00	71	Firm	[8]30	NE	White	Soft.

NE Not evaluated.
[1]See table 1 for explanation of codes.
[2]Percent weight gain of dry powder in 18 h (*29*).
[3]Ash obtained by heating dried materials at 200° C/h up to 1,000° C and soaking at 1,000° C for 1 h.
[4]Determined with dry clays, dry polymers, and wet sludges.
[5]Obtained with wet binders except as noted.
[6]Determined with briquets made of dry minus 100-mesh powders and water except as noted.
[7]Water required to obtain paste of dried, ground, minus 100-mesh material.
[8]Obtained with wet sludge.
[9]Briquets made of wet sludge.

Table 3.–Partial chemical analyses of Mesabi Range taconite concentrate, clays, pure organic polymers, and waste papermill sludges

(Clay, polymer, and sludge samples dried overnight at 75° C; taconite dried overnight 105° C)

Sample[1]	Chemical analysis, pct												LOI at indicated temperature, pct				
	Al	C	Ca	Fe	K	Mg	Mn	Na	P	S	Si	Ti	105° C	300° C	500° C	700° C	1,000° C
Taconite	<0.2	<1	<0.3	[2]65.2	<0.10	0.3	NE	0.1	<0.10	<0.10	2.6	<0.3	<0.1	NE	NE	NE	-1.7
Clays:																	
BEN17	9.6	<1	1.1	2.9	.40	1.5	NE	1.5	.02	.10	27.9	<.3	2.2	NE	NE	NE	9.7
KAOL1	21.7	<1	<.3	.4	<.10	<.1	NE	.1	<.10	<.10	21.3	.4	.2	NE	NE	NE	4.4
Polymers:																	
CMCH1	<.2	56	NE	NE	<.10	NE	NE	7.3	<.10	<.10	<.5	NE	7.7	53.1	82.5	91.8	94.9
GG211	<.2	39	NE	NE	.17	NE	NE	.1	<.10	<.10	<.5	NE	9.2	73.8	99.0	99.4	99.7
SC71	<.2	23	<.3	NE	<.10	NE	NE	<.1	<.10	<.10	<.5	NE	10.2	70.8	99.9	99.9	99.9
SWG70	<.2	41	NE	NE	NE	NE	NE	<.1	NE	NE	NE	NE	6.5	69.9	NE	99.7	99.7
Sludges:																	
WmDs1	5.0	26	1.6	1.1	.62	.6	0.04	1.0	1.90	.47	4.9	1.8	5.5	45.7	66.3	66.6	67.0
WmDs2	4.9	28	1.7	1.7	.54	.6	.04	.7	1.80	.70	5.5	NE	5.5	42.2	64.4	64.8	65.3
WpR3b	5.3	27	.5	NE	.11	.2	NE	.1	<.10	<.10	4.8	.4	6.7	61.2	75.9	76.6	77.0
WmpRs3b . .	5.3	27	.9	NE	.11	.2	NE	.3	.15	.16	5.5	NE	6.6	58.9	75.1	75.6	76.2
WpBs1	7.5	30	1.7	.6	<.10	.7	.28	.1	.51	.11	8.2	.7	6.2	NE	NE	NE	74.4
WpBs1-	8.9	34	1.9	1.0	<.10	.8	.27	.1	.56	.17	9.4	.8	18.9	NE	76.6	NE	78.2
WpBs1+ . . .	4.3	33	1.6	.7	<.10	.4	.27	.1	.42	<.10	4.5	.6	5.5	NE	85.9	NE	86.8
WpBs2	13.6	20	7.7	NE	.20	.2	NE	.1	<.10	.12	8.2	NE	1.8	18.5	31.6	41.1	42.1
WpC1	4.3	27	6.2	NE	<.10	.2	NE	.2	<.10	.13	4.5	NE	4.6	52.3	63.4	69.4	69.7
WpS1	9.6	27	.4	NE	<.10	.1	NE	<.1	<.10	.11	8.4	NE	5.0	46.5	62.3	62.9	63.5
WpSs1	11.9	28	.4	NE	.71	.1	NE	.2	.12	.18	9.2	NE	4.6	38.3	55.4	56.2	56.9

LOI Loss on ignition.
NE Not evaluated.
[1]See table 1 for explanation of codes.
[2]21.8 pct Fe^{2+}

EXPERIMENTAL METHODS

BINDER DIAGNOSTIC PROCEDURES

Diagnostic tests were conducted on the binders to determine their physical and chemical characteristics. Only brief descriptions of most of these tests are given in this report. Detailed test descriptions are provided in a previous publication (*29*).

The main binder diagnostic test used by the iron ore industry is the ASTM plate water absorption test (PWAT) (*30*). This test involves placing 2 g of minus 100-mesh binder (dried overnight at 105° C) on a filter paper, which in turn is placed on a wet ceramic brick that is partially immersed in distilled and deionized water. With the pure polymers, only 0.2 g is used and a plastic ring (5-cm diam, 6 mm thick) is placed around the sample. The percentage weight gain of the dry sample after 18 h is determined.

In this study, the weight gains of nondried materials (raw sludges) were also evaluated. These weight gain values are important in the pelletizing operations. Operators prefer binders with high PWAT values, especially when the iron ore concentrate filter cake contains about 10 pct water. When the filtering operation does not remove sufficient water, more bentonite is added to improve the pelletizing operation.

GREEN PELLET PREPARATION AND PHYSICAL TESTING PROCEDURES

Raw Material Mixing

Iron ore concentrate and the binder were blended using different mixing methods.

1. The dry-dry M method consisted of mixing 3 kg of dry concentrate with a predetermined quantity of dry binder and then dripping in 330 mL of distilled water over a period of 15 min while the mixture was stirred in a 1-ft-diam muller (M) mixer.
2. The dry-wet K method was similar to the dry-dry M method only raw sludge and a kitchen-type (K) mixer were used. When raw sludge was added, the addition level was expressed as both a wet and dry weight equivalence.
3. With the wet-dry K or wet-wet K method, wet (nominally 9 pct water) concentrate was blended with dry or wet binder in the kitchen-type mixer. The muller mixer was also used instead of the kitchen-type mixer to blend some of the samples, a method designated wet-wet M.
4. The wet-wet A method involved adding a predetermined quantity of sludge with 1.5 L of water and agitating this slurry (less than 2 pct solids) for 15 min in a flotation cell; a 2-pct-solids sludge slurry simulates a mixture presently being pumped in one papermill processing operation. Wet concentrate was then added and the slurry was blended in the agitated mixer for an additional 15 min. The slurry was then filtered. The filter cake was added to the kitchen-type mixer and blended for an additional 15 min prior to pelletizing.

Pelletizing Procedure

One-tenth of the concentrate and binder mixture (about 0.3 kg) was initially sprinkled into a 16-in-diam pelletizing disk rotating at 50 rpm to form seed pellets. Water was sprayed on the pellets and more mixture was added as needed to build up the pellet size. When the pellets reached the 7/16-in-diam size, they were removed and the undersize returned to the disk. The pelletizing procedure was continued until all the mixture was used. Only the pellets in the minus 1/2-, plus 7/16-in size range were used in the pellet evaluation tests.

Pellet Testing Procedures

Immediately after the pellets were made, the drop number and wet compressive strength of the pellets were determined. The dry compressive strengths were determined on pellets dried overnight at 105° C. The wet and dry pellets are referred to as green (nonindurated) pellets.

The wet pellets were kept in sealed containers until they were used in the shock temperature test. This test involved inserting an alumina tray of wet pellets directly into a preheated muffle furnace for 30 min at 1,000° C. Five batches of 30 pellets were heated at one time. The percentage of pellets that did not break or spall was called the survival percentage.

The pellet induration procedure involved drying wet pellets at 105° C overnight and placing them in an alumina tray. The loaded tray was inserted into a preheated muffle furnace for 30 min at 900° C to oxidize the magnetite to hematite, and then immediately placed in a second preheated muffle furnace for 15 min at 1,250° C. The tray was then removed and covered with a 900° C preheated alumina tray. The fired compressive strength of the cold pellets was determined by standard pellet testing methods. The open pore porosity was determined with a high-pressure porosimeter (up to 60,000 psig).

METALLURGICAL TESTING PROCEDURES

The metallurgical tests consisted of the reduction kinetics, reduction disintegration, and high-temperature softening-melting experiments.

The reduction tests were conducted with a thermogravimetric apparatus (*31*). The tests were conducted for 6 h at 900° C using 30 pct CO, 0.1 pct H_2, and balance N_2 (*32*). The percentage reduction was assumed to be directly related to the weight loss of the sample. The low-temperature reduction disintegration index (RDI) tests were conducted at 500° C for 1 h using 20 pct CO, 20 pct CO_2, 2 pct H_2, and balance N_2 according to ISO 4696 (*33*).

The high-temperature softening-melting tests were conducted with the equipment shown in figure 1. The furnace was heated with silicon carbide heating elements.

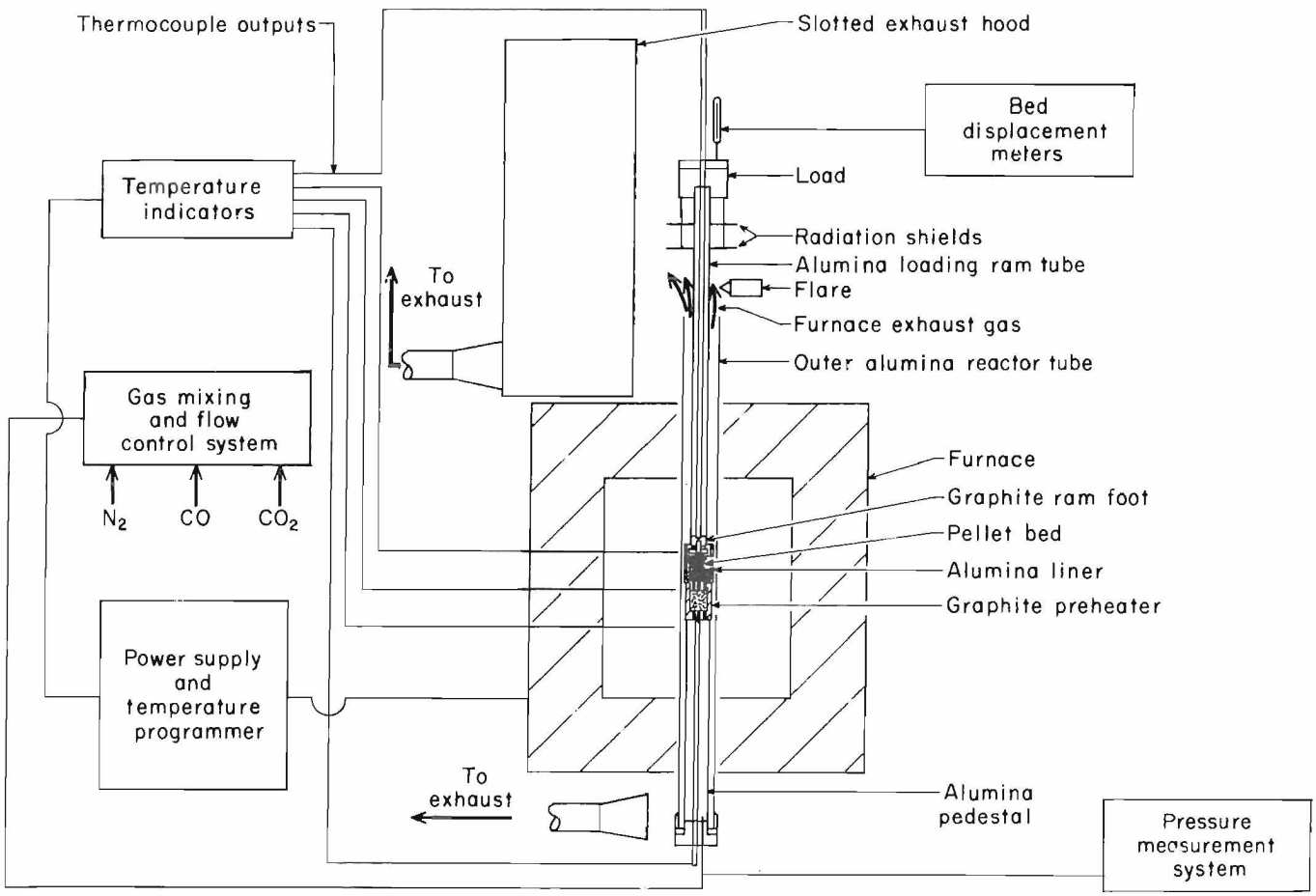

Figure 1.–Schematic diagram of high-temperature softening-melting apparatus.

A cross section of the reactor assembly is shown in figure 2. The reactor tube (99.9 pct alumina) had a 10.6-cm OD, a 9.8-cm ID, and a 1.5-m length. An alumina tube (5.0-cm OD, 4.4-cm ID, 0.6 m long) was used as a pedestal to support the graphite preheater and pellet bed.

The preheater crucible contained about 330 g of graphite chips (minus 12 mm, plus 10 mm). An alumina crucible was placed above the preheater to collect the molten pellet products. Above the preheater was a fabricated graphite holder that had 14 holes (6-mm diam) in the bottom and contained a tight-fitting alumina liner (5.7-cm OD, 5.1-cm ID, 11.0 cm long). At the bottom and inside of the alumina liner, there was a single coarse layer (about 1 cm thick and about 10 g) of minus 11-, plus 9-mm coke chips. A second layer (about 0.5 cm thick and about 5 g) of finer coke chips (minus 8 mm, plus 3 mm) was placed above the first coke layer.

The pellet bed (6.35 cm high, about 250 g of minus 7/16-, plus 3/8-in-diam fired pellets) was placed inside the alumina liner. Another 0.5-cm-thick layer (about 5 g) of the finer coke chips was placed above the pellet bed. A perforated (10 holes, 4-mm diam) graphite disk (4.5-cm diam, 1 cm thick) was placed on top of the upper layer of coke chips. A graphite foot with four toes was centered above the graphite disk and inside the alumina ram (3.7-cm OD, 3.1-cm ID, 1.4 m long). On top of the ram, a static load of 8.1 kg was used to apply a force of 0.5 kg/cm^2 on the pellet bed. The thermocouple, used for determining the pellet bed temperature, was located in the middle of the graphite foot immediately above the pellet bed.

The gas pressure drop, bed shrinkage, and temperature were continuously recorded during the high-temperature softening-melting test. The pressure drop was measured with both a pressure gauge and a linear pressure transducer. A differential transformer-type displacement transducer and a standard depth dial indicator were used to measure the shrinkage of the pellet bed. The overall measurement error was less than 1 pct.

The high-temperature softening-melting test procedure consisted of flushing the reactor with 8 SLM of nitrogen while the furnace was heated to 750° C overnight. The next morning, the gas composition was switched to 25 SLM of 24 pct CO, 16 pct CO_2, and 60 pct N_2. The furnace temperature was then increased to 1,100° C at the rate of about 3° C/min. At temperatures above 1,100° C, the heating rate was about 1° C/min and the gas mixture was 30 pct CO and 70 pct N_2. This heating rate and gas

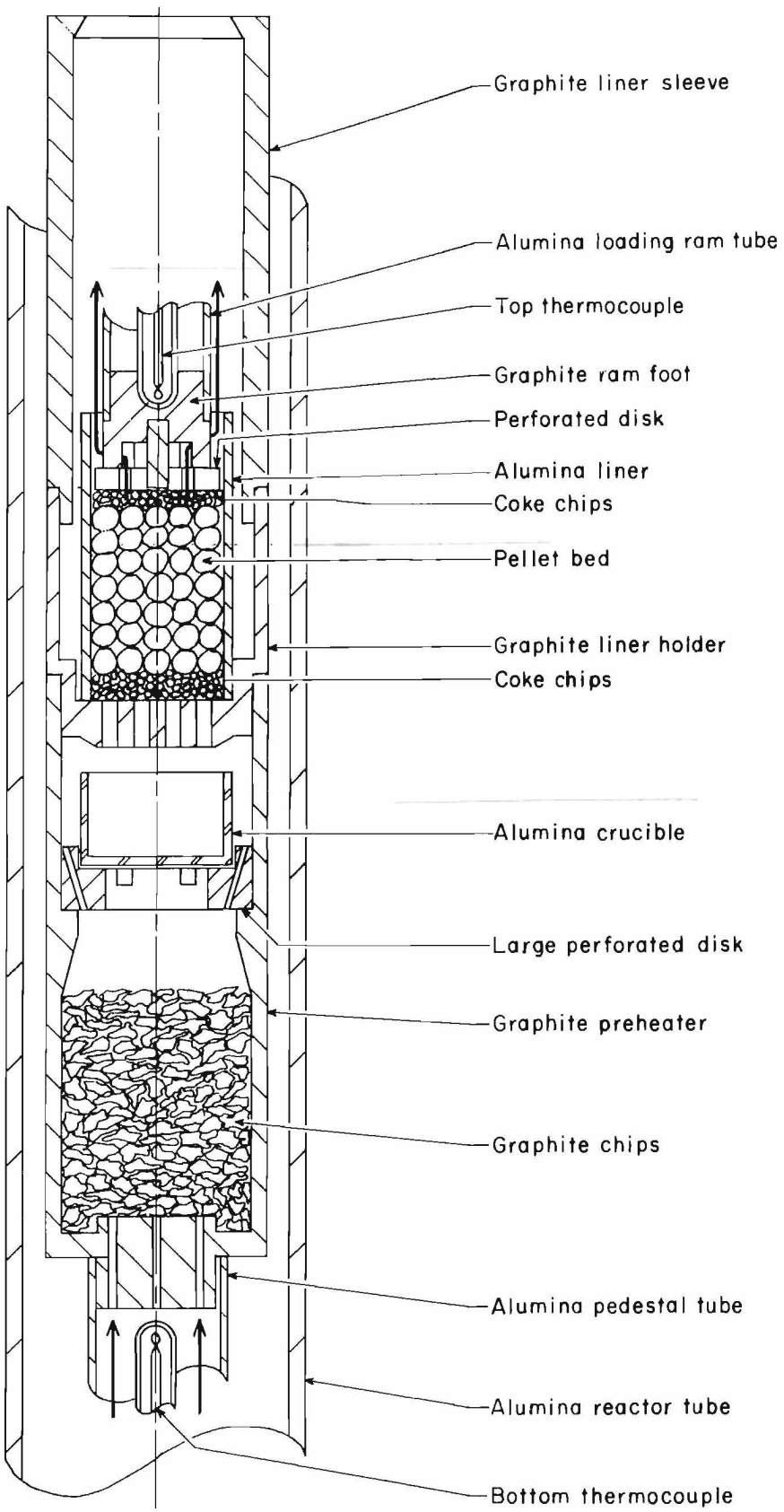

Figure 2.–Cross-sectional view of reactor section of high-temperature apparatus.

composition were maintained until the pellet bed shrinkage reached a maximum and leveled off. At this time, the furnace power was shut off and a 15-SLM N_2 flow was maintained through the pellet bed until the sample cooled to about 200° C. The softening temperature value was defined as the temperature when the pressure drop across the pellet bed reached 10 mm Hg. The shrinkage measurement included the total displacement of the support column thermal expansion plus the pellet column expansion and contraction.

EXPERIMENTAL RESULTS AND DISCUSSION

BINDER DIAGNOSTIC STUDIES

Physical Characteristics

Texture

Physical characteristics of the sludges, pure organic polymers, and clays were determined to better understand the behavior of the binders alone before they were added to the iron ore concentrate. It is well known that the conventional iron ore concentrate binder (western bentonite clay) has the following properties: (1) swells in the presence of water to form a soft, thick, and plastic paste; (2) shrinks considerably when the wet paste is dried; and (3) sinters when exposed to temperatures above about 1,000° C. Therefore, in order to compare the similarities of bentonite with sludge and its ingredients, the behavior of these materials in the presence and absence of water was determined.

Clays, pure organic polymers, and the raw municipal secondary sludges (WmDs) had fine and soft textures similar to bentonite (table 2). These wetted materials could easily be molded into a 12-mm-diam briquet without prior grinding. However, coarse and firm textures were observed with the raw primary sludges (WpC1, WpR3b, WpS1), municipal primary-secondary sludges (WmpRs), and primary-secondary sludge (WpSs1). These sludges had a high (28 pct or more) coarse fiber content (table 4). One primary-secondary sludge (WpBs2) had a fine texture and it had the lowest (9 pct) coarse fiber content of the primary-secondary sludges.

Table 4.–Partial analyses of sludge size fractions from sedimentation tests

Binder[1] size[2]	wt pct	Analysis, pct										LOI at 1,000° C
		Al	C	Ca	K	Mg	Mn	Na	P	S	Si	
WpBs2:												
Coarse fiber	9	6.1	45	3.4	0.12	<0.1	<0.02	0.07	<0.05	0.15	4.4	70.5
Fine fiber	59	11.2	20	9.4	.25	.2	<.02	.11	<.05	.13	9.7	35.5
Coarse colloid	19	14.2	15	4.5	.08	.2	<.02	.06	<.05	.16	11.0	31.6
Fine colloid	13	10.0	23	6.0	.18	.6	<.02	.51	.13	.45	8.2	42.6
WpC1:												
Coarse fiber	50	.8	42	.6	.05	.1	<.02	<.05	<.05	.13	1.2	92.3
Fine fiber	31	6.4	18	14.4	.08	.4	<.02	.25	<.05	.13	7.5	42.2
Coarse colloid	10	10.3	13	4.3	.08	.4	.02	.12	NE	.16	11.9	27.3
Fine colloid	9	5.4	23	7.5	.45	1.4	.03	2.20	NE	1.30	6.1	48.9
WmDs1:												
Coarse fiber	1	2.5	NE	2.5	NE	4.7	NE	NE	NE	NE	4.9	NE
Fine fiber	52	8.4	22	2.9	1.20	1.0	.08	1.20	1.20	.65	11.4	36.7
Coarse colloid	10	6.7	33	2.3	.57	.7	.06	.56	1.20	.87	7.4	53.7
Fine colloid	37	2.5	42	1.2	.67	.3	.03	.59	1.70	1.40	2.2	80.9
WmpRs3b:												
Coarse fiber	35	.3	51	.5	<.05	<.1	<.02	<.05	.19	.17	.4	98.5
Fine fiber	48	6.0	43	.6	.11	.2	.07	.10	.37	.32	6.9	67.1
Coarse colloid	6	11.9	30	1.0	.15	.3	.15	.20	NE	.41	12.7	42.0
Fine colloid	11	6.7	37	3.8	.50	1.1	.62	1.00	.44	1.00	7.3	58.4
WpSs1:												
Coarse fiber	28	3.2	54	.6	<.05	.1	<.02	<.05	.26	.20	3.3	85.9
Fine fiber	48	15.8	22	.5	.11	.1	<.02	.10	.30	.20	13.7	38.5
Coarse colloid	14	16.0	18	.7	.10	.2	.05	.16	.36	.28	15.2	32.2
Fine colloid	10	11.0	22	3.3	.46	1.3	.04	1.60	NE	1.40	10.0	45.8

LOI Loss on ignition.
NE Not evaluated.
[1]See table 1 for explanation of codes.
[2]Coarse fiber, fine fiber, and coarse colloid fractions are sediments removed after 1, 18, and 168 h of settling, respectively; fine colloid fraction is material remaining in suspension after 168 h.

Variation in the coarse fiber content is probably related to the type of wood processing and papermaking operation that occurred where the sludge was produced. Also some papermaking companies pulverized the wood at one location and transported only the fine pulp to a specialty paper operation at another location. This type of operation may generate very little primary sludge and the majority of its sludge would be in the finely divided form. Some companies intentionally change the ratio of primary to secondary (fast and slow settling materials, respectively) sludge mix to improve dewatering of the secondary sludge.

A high colloid content (>30 pct) and a low coarse fiber content (<10 pct) was obtained from the fine texture raw sludges (WpBs2 and WmDs1, table 4). The high colloid content of these sludges probably results from the high clay and organic polymer contents. Organic polymers and clay are used for coating paper, but some of this material is lost and ends up in the sludge. The coarse colloidal size particles and fine fiber fractions appear to contain clay, as indicated by the high aluminum and silicon elemental concentrations and low LOI (table 4). In general, the aluminum and silicon contents were greater in the colloidal size fraction (table 4) than in the fiber fraction or in the original nonsized sludge samples (table 3). The WpB and WpS sludges had the highest clay contents as indicated by the high aluminum and silicon analyses (table 3). The high aluminum and silicon contents probably result from the large quantity of kaolin clay used in the paper-coating operation.

Water Content and Bulk Density

The raw municipal secondary paper sludge (WmDs1) contained 82 pct water, which is about 10 pct more water than that contained in the wettest primary sludge (table 2). The WmDs1 sludge also contained the highest colloid content (table 4). It is well known that colloidal sludges are more difficult to dewater than fibrous sludges. The municipal primary-secondary sludges (WmpRs) contained slightly less water (about 77 pct); the municipal fraction of this sludge was about 5 pct. The same sludge without the municipal waste added (WpR3b) contained slightly less water (73 pct). These results suggest that dewatered sludges containing municipal wastes (fine-textured materials) will hold more water.

Two of the raw primary sludges (WpC1 and WpS1) had low water contents (62 and 65 pct, respectively). One reason that the WpC1 sludge had a low water content is probably due to its high amount of coarse fiber (50 pct), as shown in table 4. The low water content of WpS1 sludge may be partially explained by its high kaolin clay content, as suggested by the high aluminum and silicon and low alkali analyses (tables 3 and 4). Table 2 indicates that kaolin clay has a low (36 pct) water of plasticity and also a low (50 pct) PWAT value; the water of plasticity was defined as the minimum quantity of water required to completely wet the dry powder to form a paste. These observations suggest that dewatered sludges containing large amounts of fiber and kaolin clay contain less water.

A major portion of sludge is water and therefore the bulk density is similar to water (table 2). In general, the bulk density of sludge is slightly less than that of bentonite, while the gelled organic polymers have bulk densities about 30 pct lower than bentonite.

Hydration

When dry ground sludges were slowly rehydrated by adding water, less water was required to make the same paste consistency as was present in the raw sludges. For example, the raw WmDs1 sludge contained 82 pct water while the quantity of water required to obtain about the same soft texture paste with the WmDs1 sludge dried at 75° C was 43 pct (table 2). Most of the raw sludges became very hard on drying, and grinding these hard materials to minus 100 mesh was insufficient treatment to cause them to completely rehydrate in cold water. In order to get complete rehydration of some of the dried organic materials, they may have to be reprocessed as is required in gelling starch.

The quantity of water required to make a thick paste from dried and ground sludges was about the same as that required with bentonite and organic polymers. The sludges had low PWAT values (table 2). The nongelled starch (SC71) and kaolin also had low PWAT values but did not require much water for making a thick paste. Therefore the PWAT values appear to be a poor indicator of the water required to make a thick paste from the papermaking constituents and dried sludges.

The quantity of water in some colloidal hydrogel binders was determined after the PWAT experiment was completed. Bentonite had a PWAT value of 940, which indicates that the wet gel contained approximately 90 pct water. The CMCH1 polymer contained over 97 pct water and had a PWAT value of 3,260. Sludges are known to contain both clays and organic polymers, which is suggested by the chemical analyses and high fine colloid contents (table 4). The high PWAT and percent water values for these pure hydrogels helps to explain why sludges have high water contents (table 2).

The raw sludges had very low PWAT values (table 2) and therefore have considerably less water absorption capacity (drying power) than bentonite and gelled polymers. Thus, sludge binders may not be effective in pelletizing operations that have a very wet filter cake concentrate. In these iron ore operations, bentonite or some other material may have to be added to absorb the excess water.

The hydration and dehydration behavior was studied by making briquets out of the sludges and their constituents. The briquets were heated at 75° C overnight and the volumetric shrinkages of the cold briquets were determined. High shrinkages (>65 pct) were obtained when briquets were made with raw secondary sludge (WmDs), bentonite, and the gelled polymers (table 2). Briquets made with dried and ground sludges, kaolin clay, and nongelled starch had a lower shrinkage (<50 pct). The degree of shrinkage of the dried materials appeared to correlate with the PWAT values.

Chemical Characteristics

The chemical analyses of the sludges, dried at 75° C, are given in table 3. The LOI was determined at different temperatures in an oxidizing atmosphere. Most of the relative weight loss occurred at 300° C, which probably resulted from the combustion of the organic materials. More weight loss was observed at 105° C with the minus 400-mesh size fraction of the WpBs1 sludge than the plus 400-mesh fraction, which suggests that the fine materials held more water. With the WpBs2 sludge, about 25 pct of the loss occurred between 500° and 700° C, which indicates that the material did not burn readily or that considerable water was held by hydrous clays; the incomplete breakdown of the materials at temperatures below 700° C may be an asset in the pellet induration operation because some binding material is necessary until the slag bonding temperature is obtained.

The WpBs2 sludge had the lowest LOI at 1,000° C of all the sludges (table 3) and therefore probably the highest ash content; the percent ash is defined as 100 minus the LOI value at 1,000° C. A high ash content suggests the presence of clay, which was confirmed by the high aluminum and silicon contents.

Table 5 contains the chemical analyses of the sludge ashes obtained at 1,000° C. The primary WpC1 and secondary municipal WmDs2 sludge ashes had the lowest aluminum and silicon contents, and therefore most likely contained the lowest clay contents. These ashes, along with the ash from WpBs1 sludge, contained high percentages of calcium, which probably resulted from the use of lime for pH adjustment in the papermaking process. These high calcium contents and the magnesium content in WmDs2 may be favorable properties because they can act as fluxes in the pellet. However, the high sodium and potassium contents in WmDs2 may be harmful because alkali compounds are known to lower the melting temperature of refractory oxides. More fusion was obtained with this sludge and the ash was brittle (table 2). The WmDs2 and WmpRs3b ashes had higher phosphorous contents, which is expected from sludges containing municipal wastes. The ash from WmDs2, WpBs1, and WpC1 sludges had high titanium contents, which probably resulted from the use of titanium oxide in the papermaking process.

GREEN PELLET PHYSICAL PROPERTIES

Baseline Binders

The carboxyl methyl cellulose sample (CMCH1) was the first polymer investigated because this type of material recently received the most attention in the iron ore industry (*3*). The green (wet or dried at 105° C) physical properties of pellets made with this binder were compared to properties of pellets made with the conventional bentonite and paper sludge binders.

The results in table 6 indicate that pellets made with 0.1 pct CMCH1 binder have strengths better than those made with 0.5 pct bentonite but not as good as those made with 1 pct bentonite (tests 2, 3, and 5). In this study, the minimum acceptable mean target values for green pellets were arbitrarily set at drop number, 4; and dry compressive strength, 4 lb/p. These values were higher than the results obtained with no binder (table 6) but lower than with 0.5 pct bentonite. The target values are given in the headnote of table 6. No target value was set for the wet compressive strength because this value was found not to be very meaningful in this comparative study.

Sludge Binders

Influence of Mixing Methods

Several different methods were used to mix the binder with the iron ore concentrate before pelletizing. The first method involved blending dry concentrate and dry ground binders in a muller mixer. With most of the sludge binders tested, this dry-dry M mixing method generally resulted in pellets with compressive strengths above the target values for addition levels between 1 and 2 pct (dry weight basis) sludge (table 6, tests 14, 15, 22, 23, 33, 45, and 50). A graphical display of the importance of the binder addition with a dried sludge (WmpRs1d) is shown in figures 3 and 4. It is apparent from these results that more than 1 pct (dry basis) binder was generally required to reach the drop number target value. The low drop numbers with dried sludge binders are probably due to their low degree of rehydration and/or the shorter sludge fiber length; the dried sludge was ground to minus 100 mesh, which decreased the fiber length but improved the ease of mixing. The organic polymers and bentonite have higher PWAT values than dried sludge and therefore have relatively higher drop numbers (fig. 3).

The dry-wet K mixing method involved mixing dry concentrate with raw (wet) sludge in a kitchen-type mixer. The initial wet sludge tests were conducted with 5 pct wet (about 1-2 pct dry) weight of raw sludge. This addition level resulted in pellets which met the target values (tests 20, 26, 43, 46, 52, and 61). These results indicate that wet sludge is more effective than dry sludge. Even though direct comparison cannot be made, pellets made with wet sludge D binder, generally, had the best green properties. Sludge D also contained the greatest percentage of fine colloidal organic materials.

The wet-wet K mixing method involved blending wet filter cake concentrate with wet raw sludge in a kitchen-type mixer. With this wet method, slightly better results were obtained than with the dry-dry M method (tests 17 versus 14, and 29 versus 33). When the wet concentrate-raw sludge method was used, the pellets had a slightly higher moisture content and correspondingly higher drop numbers. Adding bentonite to this mixture slightly improved the dry compressive strength (test 35 versus 28).

Table 5.–Partial chemical analyses of sludge ashes, percent

Binder[1]	Al	C	Ca	K	Mg	Na	P	S	Si	Ti
WmDs2	13.2	<0.1	4.3	1.4	1.5	1.6	2.30	0.03	17.3	5.0
WmpRs3b	18.2	<.1	2.3	.3	.6	.3	.57	.12	22.6	1.5
WpR3b	18.1	<.1	1.9	.3	.6	.3	.22	.15	23.2	1.3
WpBs1	17.3	<.1	12.0	.5	.4	.1	.28	.03	15.5	3.1
WpC1	13.1	<.1	17.5	.1	.7	.4	.32	.22	14.3	9.8
WpSs1	20.6	<.1	1.1	.2	.2	.2	.42	.04	32.9	1.0

[1]See table 1 for explanation of codes.

Table 6.–Physical properties of pellets made with different binders

(Target values: <2.0 pct dry addition, 9.0 pct H_2O, wet drop >4.0, >4-lb/p dry compressive strength, >400-lb/p fired compressive strength, >95 pct survival)

Test	Binder[1]	Addition, pct		Pellet		Drop No.	Pellet strength, lb/p			Survival,[2] pct
		Dry[3]	Wet[4]	Method[5]	H_2O, pct		WCS	DCS	FCS	
1	None	0.0	NAp	Dry-dry M	6.6	3.2	3.1	2.3	375	NE
				CLAYS						
2	BEN17	0.5	NAp	Dry-dry M	7.0	4.2	1.6	4.9	420	100
3	BEN17	1.0	NAp	Dry-dry M	7.6	9.2	4.1	20.9	737	86
4	KAOL1	1.0	NAp	Dry-dry M	7.2	3.9	2.8	4.4	855	NE
				PURE ORGANIC POLYMERS						
5	CMCH1	0.1	NAp	Dry-dry M	9.0	7.0	4.1	7.0	673	NE
6	CMCH1	.2	NAp	Dry-dry M	8.9	15.2	3.8	20.6	712	100
7	GG211	.1	NAp	Dry-dry M	9.7	11.9	2.8	5.9	644	100
8	GG211	.3	NAp	Dry-dry M	11.0	>25.0	3.7	27.4	397	100
9	SC71	.1	NAp	Dry-dry M	8.1	3.2	2.0	5.8	669	NE
10	SC71	.3	NAp	Dry-dry M	8.0	3.0	2.0	6.5	621	NE
11	SWG70	.1	NAp	Dry-dry M	9.7	4.0	1.5	3.2	663	96
12	SWG70	.2	NAp	Dry-dry M	8.4	4.5	2.6	13.9	620	NE
13	SWG70	.3	NAp	Dry-dry M	8.4	6.2	2.7	28.6	NE	NE
				MUNICIPAL AND PRIMARY-SECONDARY PAPER SLUDGE D						
14	WmDs2d	1.0	NAp	Dry-dry M	8.0	4.7	1.5	3.0	566	100
15	WmDs2d	2.0	NAp	Dry-dry M	7.9	5.4	2.9	4.5	445	100
16	WmDs2	.5	3.0	Wet-wet K	8.3	6.4	3.4	11.3	674	100
17	WmDs2	.9	5.0	Wet-wet K	9.0	6.6	2.6	11.7	571	100
18	WmDs2	1.2	7.0	Wet-wet K	8.8	17.8	3.7	26.2	715	100
19	WmDs2	.9	5.0	Wet-wet A	9.2	11.0	3.1	11.9	678	100
20	WmDs1b	.9	5.0	Dry-wet K	8.3	7.0	2.5	18.1	656	NE
21	WmDs1-5	.9	5.0	Dry-wet K	9.3	5.5	2.0	8.7	489	100
				MUNICIPAL AND PRIMARY-SECONDARY PAPER SLUDGE R						
22	WmpRs1d	1.0	NAp	Dry-dry M	8.6	3.6	1.9	4.4	492	NE
23	WmpRs1d	2.0	NAp	Dry-dry M	9.4	6.5	2.1	5.8	448	NE
24	WmpRs1d	5.0	NAp	Dry-dry M	11.7	11.4	1.9	7.3	293	NE
25	WmpRs2b	2.0	8.2	Dry-wet K	10.3	7.2	2.3	5.8	314	NE
26	WmpRs3b	1.4	5.0	Dry-wet K	9.7	9.3	2.2	7.8	540	NE
27	WmpRs3b	2.8	10.0	Dry-wet K	13.7	>25.0	1.8	7.3	263	100
28	WmpRs3b	.8	3.0	Wet-wet K	9.0	4.4	2.3	5.7	464	100
29	WmpRs3b	1.4	5.0	Wet-wet K	10.0	9.6	2.8	5.8	441	100
30	WmpRs3b	1.4	5.0	Wet-wet A	10.4	13.2	3.1	7.5	446	100
31	WmpRs3b	2.0	7.0	Wet-wet A	11.1	21.6	4.1	10.2	419	100
32	WmpRs3b	2.8	10.0	Wet-wet A	11.4	23.4	3.6	10.5	377	100
33	WmpRs3bd	1.0	NAp	Dry-dry M	9.3	5.0	2.3	3.7	541	100
34	WmpRs3br	1.4	5.0	Wet-wet A	11.6	20.7	3.1	8.2	442	100
35	WmpRs3b/B	.6	2.0	Wet-wet K	8.3	4.4	2.3	6.7	503	100

See explanatory notes at end of table.

Table 6.–Physical properties of pellets made with different binders–Continued

(Target values: <2.0 pct dry addition, 9.0 pct H_2O, wet drop >4.0, >4-lb/p dry compressive strength, >400-lb/p fired compressive strength, >95 pct survival)

Test	Binder[1]	Addition, pct		Pellet		Drop No.	Pellet strength, lb/p			Survival,[2] pct
		Dry[3]	Wet[4]	Method[5]	H_2O, pct		WCS	DCS	FCS	
	MUNICIPAL AND PRIMARY-SECONDARY PAPER SLUDGE R (PARTIALLY DRIED)									
36	WmpRs3bP	1.3	4.0	Wet-wet A	9.5	9.4	2.8	6.0	628	100
37	WmpRs3bP	1.7	5.1	Wet-wet A	11.0	>25.0	3.6	10.0	533	100
38	WmpRs3bPt	1.2	3.6	Wet-wet A	10.1	14.8	2.9	6.2	547	100
39	WmpRs3bP1S	1.4	3.4	Wet-wet K	10.8	10.3	2.4	2.8	306	100
40	WmpRs3bP7S	2.0	4.7	Wet-wet K	10.7	16.8	2.4	9.1	479	100
41	WmpRs3bP7L	.5	1.1	Wet-wet K	8.2	3.7	2.0	3.9	677	100
	PRIMARY PAPER SLUDGE R									
42	WpR2	2.7	9.5	Wet-wet A	11.0	24.2	3.6	15.7	557	100
43	WpR3b	1.4	5.0	Dry-wet K	9.7	18.0	4.8	8.4	546	NE
44	WpR3b	1.4	5.0	Wet-wet A	10.1	18.1	3.7	7.8	600	100
	PRIMARY-SECONDARY PAPER SLUDGE B									
45	WpBs1d	1.0	NAp	Dry-dry M	8.2	3.8	1.9	5.9	455	NE
46	WpBs2	2.1	5.0	Dry-wet K	8.6	5.6	2.0	6.9	573	NE
47	WpBs2	2.1	5.0	Wet-wet K	7.9	5.7	2.5	7.1	609	100
48	WpBs2	3.1	7.0	Wet-wet K	8.6	7.6	3.0	8.6	603	100
49	WpBs2	2.1	5.0	Wet-wet A	8.7	6.6	2.8	6.3	665	100
	PRIMARY PAPER SLUDGE C									
50	WpC1d	1.0	NAp	Dry-dry M	8.5	4.7	2.2	4.0	518	100
51	WpC1	.8	2.0	Wet-wet K	9.2	6.3	2.3	4.0	400	[6]57
52	WpC1	1.9	5.0	Dry-wet K	11.1	12.4	1.9	6.6	335	100
53	WpC1	1.9	5.0	Wet-wet K	10.6	11.2	1.8	5.8	293	[6]89
54	WpC1	1.9	5.0	Wet-wet M	10.7	8.9	2.3	5.7	340	[6]64
55	WpC1	1.2	3.3	Wet-wet A	9.8	13.4	3.8	8.1	484	100
56	WpC1	1.9	5.0	Wet-wet A	10.3	23.2	3.8	9.2	405	100
57	WpC1	2.8	7.0	Wet-wet A	12.4	>25.0	3.4	9.8	387	100
	PRIMARY PAPER SLUDGE C (ROD MILL GROUND)									
58	WpC1r	0.1	0.3	Wet-wet A	8.4	4.0	2.0	3.0	636	100
59	WpC1r	.7	1.8	Wet-wet A	9.0	6.6	2.6	5.2	595	100
60	WpC1r	1.4	3.6	Wet-wet A	12.7	>25.0	2.5	11.6	576	100
	PRIMARY PAPER SLUDGE S									
61	WpS1b	1.7	5.0	Dry-wet K	10.3	15.8	3.7	8.7	542	NE
	PRIMARY-SECONDARY PAPER SLUDGE S									
62	WpSs1	1.3	5.0	Wet-wet K	9.6	9.6	2.6	7.3	534	NE
63	WpSs1-5	1.3	5.0	Wet-wet K	9.4	6.4	2.6	5.1	485	100
64	WpSs1b	1.3	5.0	Wet-wet K	10.1	11.3	3.4	7.6	568	100

DCS Dry compressive strength.
FCS Fired compressive strength.
NAp Not applicable.
NE Not evaluated.
WCS Wet compressive strength.
[1]See table 1 for explanation of codes.
[2]Percentage of wet pellets that did not break (or spall) when rapidly heated to 1,000° C.
[3]Sludge dried at 75° C overnight and ground to minus 100 mesh. Dry equivalent weight of wet sludge.
[4]Wet sludge.
[5]1st word describes iron ore concentrate, 2d word describes binder, A–agitator, K–kitchen-type mixer, M–muller mixer.
[6]Pellets showed surface spalling but none were broken.

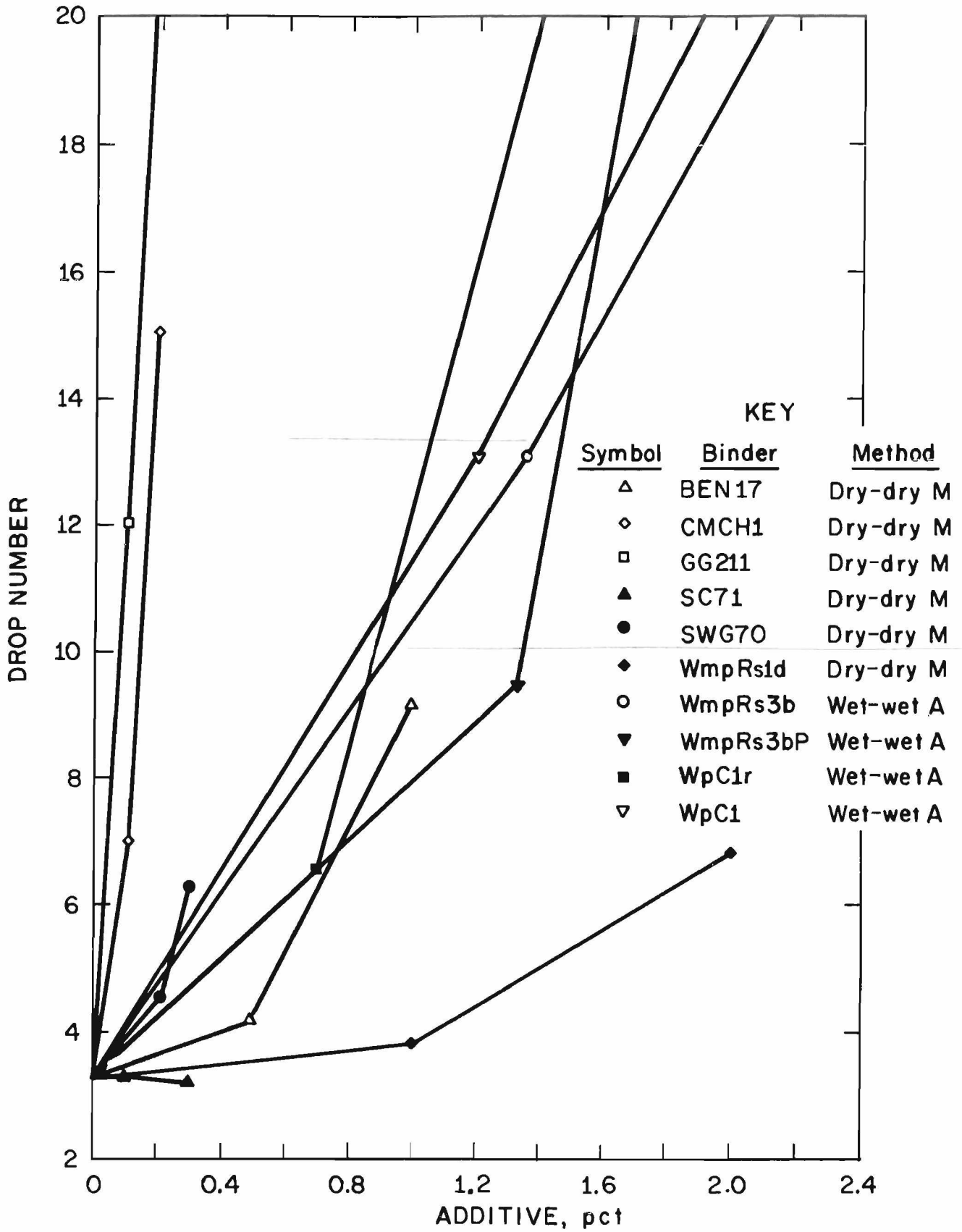

Figure 3.–Influence of binder addition level (dry equivalent weight) on pellet drop number.

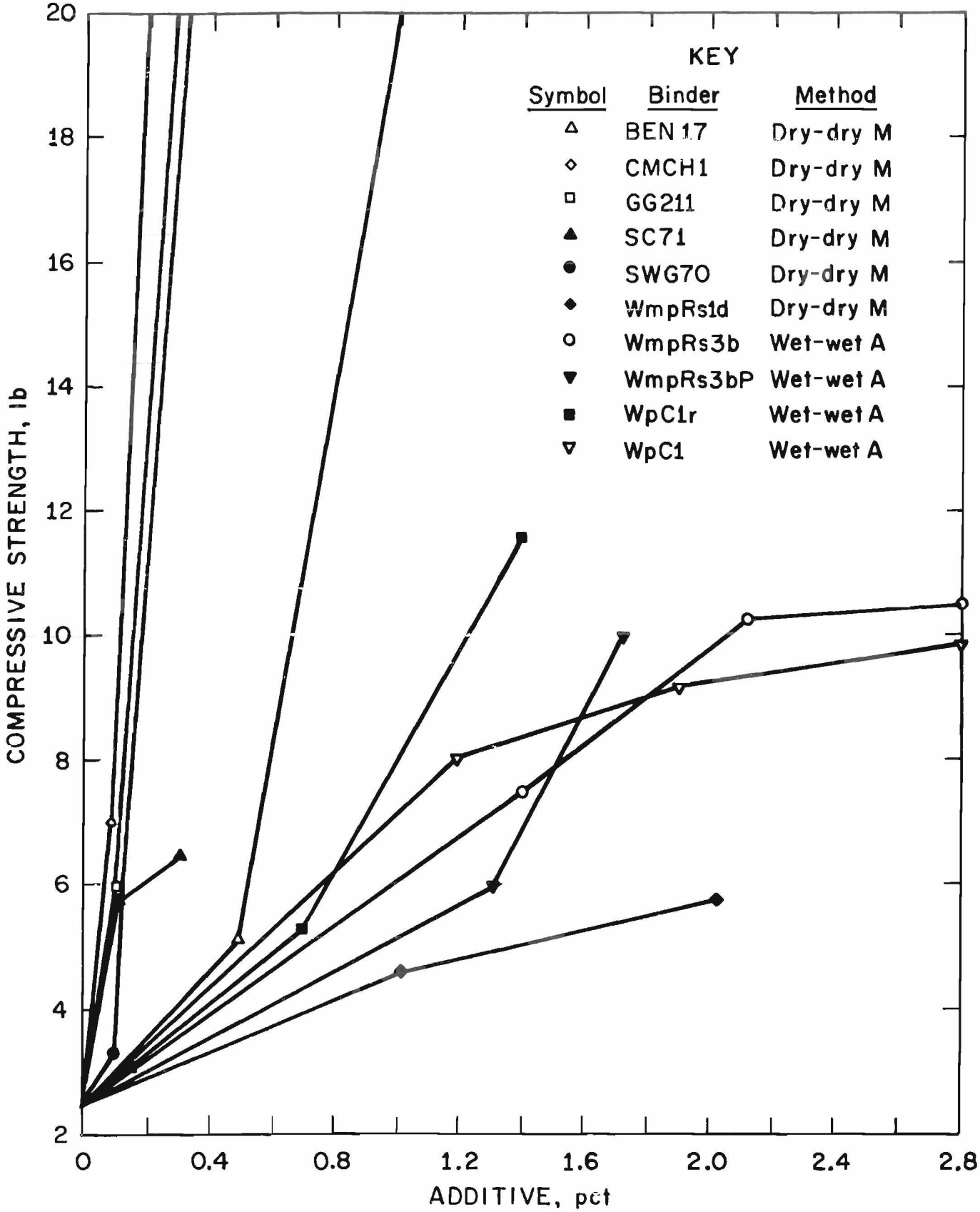

Figure 4.–Influence of binder addition level (dry equivalent weight) on pellet dry compressive strength.

The wet-wet M mixing method is similar to the wet-wet K method except the muller mixer is used in place of the kitchen-type mixer. The muller mixer has a higher shearing action on the sludge fibers than the kitchen-type mixer, possibly resulting in a more homogeneous mixture with the sludge containing the greatest percentage of coarse fibers. With this method, it was difficult to visually find sludge material in the wet pellets, while some was occasionally observed with the kitchen-type mixer method. However, preliminary results indicate that the pellet properties with the muller mixer were not quite as good (tests 53-54) but further research would be needed to verify this observation.

The wet-wet A mixing method involved agitating the sludge at 2 pct solids for 15 min and then adding the wet concentrate. This slurry was blended for another 15 min and then filtered. With this mixing method, better green physical properties were generally obtained than with the nonagitated sludge mixing methods. The better results were attributed to the vigorous agitation that broke up the sludge clumps and thereby improved the mixing. The agitation method was modified by first breaking up the sludge clumps by pushing them through a 4-mesh screen before adding them to the agitated mixer. Tearing up the sludge binder in this manner resulted in slightly better pellet drop numbers (tests 38 versus 36). The agitation method required a filtration time about three times longer (about 6 min) than was required when the concentrate was filtered alone.

In order to further determine the influence of fiber breakup, raw sludge was wet ground in a rod mill for 1/2 h at 2 pct solids. The sludge slurry and the iron ore concentrate were then blended in the agitated mixer, filtered, and the filter cake pelletized. This procedure produced pellets with the best green physical properties with sludge C (tests 59 and 60), which was difficult to mix with the other methods. However, slurries containing sludge required longer filtration times.

Better green pellet properties were obtained with the wet than with the dry grinding method (test 60 versus 50). The poorer results with dried and ground sludge is probably related to its lower degree of hydration (table 2).

With all the mixing methods, the green pellet target values were generally met with all the sludges and fairly homogeneous sludge-taconite concentrate mixtures were obtained. Sludge C was the most difficult to mix and it contained the highest portion (50 pct) of coarse fibers (table 4). With this sludge, clumps were observed in the wet pellets but most of the green pellet target values were still met at all addition levels. Sludge D contained the lowest coarse fiber content (1 pct) and was the easiest to use to obtain a homogeneous mixture with the concentrate. However, the D sludge also contained the most water and more energy would be required to dry the pellets.

Sludge Addition Level

The green strength target values were generally obtained at the 5 pct raw (about 1-2 pct dry) sludge addition level with all the sludges evaluated. As the sludge addition level was increased, both the pellet drop numbers (fig. 3) and the dry compressive strengths (fig. 4) increased. With the WpC1 and WmpRs3b raw sludges, the dry compression strength leveled off at about the 2 pct dry equivalent addition level (fig. 4). Partially drying (from 77 to 33 pct water) WmpRs3b sludge (table 6, tests 36 and 37 versus 30 and 31) did not have a major effect on the binding properties, but complete drying resulted in weaker pellets (test 33). With all the sludge binders, the pellets were almost as easy to make as with bentonite.

With the nonagitated mixing methods, the dry weight equivalent results shown in table 6 and figures 3 and 4 indicate that about two times more raw sludge is required to reach the target physical properties as with bentonite. The value of two can be used for both the weight or the volume comparison as both of these binders have similar bulk densities (table 2). On a weight basis, the gelled organic polymer binders were about 10 times more effective than raw sludge and about 15 times more effective on a volume basis.

Sludge Aging Studies

Sludges without biocide that were not stored in the refrigerator formed a green mold after about 1 week in an open container at ambient room conditions. The results with sludge D (table 6, test 20 versus 21) and sludge S (test 62 versus 63) indicate that biodegradation decreased the effectiveness of the dry binding strength. After 1 year, sludge without biocide stored in the refrigerator had about the same pellet binding properties as the same sludge with biocide stored at ambient conditions (test 62 versus 64).

Binding Properties of Sludge Size Fractions

Tests were conducted to determine the relative effectiveness of the fibrous and colloidal size fractions of the sludge, which should help delineate the best sludge components. The WmpRs3bP sludge was wet rod mill ground and the slurry allowed to settle. Sediments were removed after 1 and 7 days, and the liquid suspension was removed after 7 days. These fractions were dried at 75° C until thick pastes were obtained.

The three pastes were each mixed with the same quantity of iron ore concentrate and the mixtures pelletized. The binder addition level with the different fractions (table 6, tests 39-41) varied because the quantity of solids obtained from each fraction was different. Even though the 7-day suspension was used at the lowest binder addition level, it had considerably better dry binding properties

than the sediment removed the first day (test 41 versus 39). The 7-day suspension probably contained the greatest portion of organic polymers, which are very effective for gluing together the taconite concentrate particles (tests 5-13).

FIRED PELLET PROPERTIES

Shock Survival

Essentially no breakage or spalling was observed during the 1,000° C shock temperature test for pellets made with most of the sludges or pure organic polymer binders, but 14 pct breakage (86 pct survival) occurred with 1 pct bentonite binder pellets (table 6, test 3). Surface spalling occurred with the pellets made with WpC1 raw sludge binder using the nonagitated mixing methods (tests 51, 53, and 54). This sludge contained the largest quantity (50 pct) of coarse fibers. The surface spalling may be due to the combustion of large sludge fiber clumps located near the outside of the pellet. No surface spalling was obtained when the sludge was reslurried in the agitating mixer (tests 55-57).

Compression Strength

The target fired compressive strength (FCS) of 400 lb/p was generally obtained with all sludge binder pellets at dry equivalent addition levels of 2 pct or less except with the coarse fiber sludge C (table 6, tests 52-54) and the coarse sediment fraction of sludge R (test 39). At the 2.8-pct or greater addition level, the target FCS value was not obtained (tests 24, 27, 32, and 57). In general, the FCS values decreased with increasing quantities of sludge (tests 22-24, 28-29, and 30-32). The opposite behavior was observed with bentonite (tests 2 and 3). This binder contains more aluminum and silicon compounds than the raw sludges (table 3), which results in more slag bonding and correspondingly stronger fired pellets with higher addition levels.

Reduction Kinetics

The reduction-time dependence data for sludge binder pellets were compared with those for bentonite binder pellets. The relative reducibilities were expressed by three different indexes: percent reduction after 3 h (R-3), percent reduction per minute at 40 pct reduction (R_{40}), and the time to reach 90 pct reduction (t_{90}).

The results in table 7 indicate that if the target level was met with the R_{40} index, it was also generally met by the other two reducibility indexes. The reducibility with all the sludge binder pellets was higher than the pellets made with 0.5 or 1 pct bentonite binder (figs. 5-9, table 7). The lowest reduction rates of all the sludge pellets were obtained with the sludge D, which had the lowest (1 pct) coarse fiber content (table 4) or the highest (47 pct) colloid content. This sludge also had the most alkali in the ash (table 5). The addition of alkali is known to decrease the sintering temperature and reducibility of pellets. The reducibility decreased when the raw sludge D was dried (fig. 7). Also, biodegradation of the sludge at ambient conditions decreased the reducibility (fig. 9, table 7, test 62 versus 63).

In general, the reducibility increased with increasing sludge addition level (fig. 8, table 7), which is the opposite behavior observed with bentonite binder (fig. 5). Bentonite is a sodium aluminum silicate (table 3) and it increases the slag bonding of the fired pellets. Therefore, the residue that remains after the binder is calcined can decrease the reduction kinetics as suggested by the high reducibility with no binder (table 7, test 1). Preliminary results indicate that when bentonite is added to the sludge, a slightly lower reducibility is obtained than with sludge alone (test 35 versus 28) but higher than with bentonite alone (tests 2 and 3).

Pellet Porosity

Pellet porosity influences reducibility as well as the pellet physical properties. Binders with high organic and hydrogel contents should result in more porous pellets. Higher pellet porosities and reducibilities were obtained with the sludge binders than with bentonite (table 7). The highest porosity (38 pct) was obtained with the pellets containing a high level of raw sludge binder (test 27). The porosity of these pellets was so great that the fired strength target value was not obtained (table 6). These pellets also contained a high moisture level. An optimum sludge addition level and moisture content appears necessary to produce the best pellets.

In addition to determining the total porosity of the open pores, the pore size distributions of pellets made with bentonite and sludge R binders were also evaluated. The pore diameters were plotted against the unit weight pore volumes (density) and the differentiated curves are shown in figure 10. It is apparent from these data that the pellets made with bentonite binder had a maximum pore density at a pore size of about 2 μm, while with the sludge R binder the maximum was at a pore size of 4 μm. Also, the area under the curve with the sludge R was considerably greater than with the bentonite, which is in agreement with the total porosity data (table 7).

The greater porosity of the pellet made with sludge was also evident from the photomicrographs (fig. 11) of the polished cross sections of the pellets. The sludge binder pellet (fig. 11*D*) had elongated dark areas (capillary pores) that may have been left by the combustion of fibers. The light colored areas indicate the presence of hematite. Essentially no residual magnetite was observed. Chemical analyses of the fired pellets showed that the ferrous and gangue contents were higher with the pellets made with 1 pct bentonite than those made with sludge binder (table 8).

Table 7.–Metallurgical properties of selected pellets made with different binders

(Target values: <2.0 pct dry addition, >78.0 pct reduction after 3 h, >0.43 pct/min reduction rate at 40 pct reduction, <225 min to reach 90 pct reduction, >92.0 pct plus 6.3-mm and <5.0 pct minus 0.5-mm particle production during RDI test, >24.0 pct porosity)

Test	Binder[1]	Dry addition, pct	R-3, pct	R_{40}, pct/min	t_{90}, min	RDI, pct[2] +6.3 mm	RDI, pct[2] -0.5 mm	Porosity, pct
1	None	0.0	91.0	0.69	178	NE	NE	21.1
				CLAYS				
2	BEN17	0.5	70.1	0.35	269	NE	NE	NE
3	BEN17	1.0	68.6	.31	288	98.2	0.9	20.8
				PURE ORGANIC POLYMERS				
5	CMCH1	0.1	83.2	0.50	216	NE	NE	NE
7	GG211	.1	81.3	.48	222	NE	NE	NE
8	GG211	.3	87.3	.59	194	NE	NE	NE
12	SWG70	.2	80.4	.43	224	NE	NE	NE
				MUNICIPAL AND PRIMARY-SECONDARY PAPER SLUDGE D				
14	WmDs2d	1.0	75.2	0.39	243	NE	NE	NE
16	WmDs2	.5	78.7	.44	234	NE	NE	24.4
17	WmDs2	.9	78.4	.43	232	97.3	1.7	NE
18	WmDs2	1.2	70.1	.34	270	NE	NE	NE
19	WmDs2	.9	77.9	.44	243	NE	NE	NE
20	WmDs1b	.9	77.0	.43	242	97.8	1.8	24.8
21	WmDs1-5	.9	81.6	.48	223	NE	NE	NE
				MUNICIPAL AND PRIMARY-SECONDARY PAPER SLUDGE R				
22	WmpRs1d	1.0	86.4	0.56	203	95.0	3.9	NE
23	WmpRs1d	2.0	90.9	.66	175	96.8	2.8	31.8
24	WmpRs1d	5.0	96.0	.80	131	NE	NE	NE
25	WmpRs2b	2.0	91.6	.59	174	NE	NE	NE
26	WmpRs3b	1.4	88.0	.58	192	92.7	3.1	NE
27	WmpRs3b	2.8	95.1	.68	155	92.8	6.5	37.6
28	WmpRs3b	.8	84.9	.52	206	96.7	2.6	28.4
31	WmpRs3b	2.1	88.6	.54	188	NE	NE	NE
33	WmpRs3bd	1.0	73.5	.37	248	NE	NE	NE
34	WmpRs3br	1.4	86.4	.53	200	95.8	4.1	NE
35	WmpRs3b/B	.6	79.0	.44	230	NE	NE	NE
				MUNICIPAL AND PRIMARY-SECONDARY PAPER SLUDGE R (PARTIALLY DRIED)				
37	WmpRs3bP	1.7	92.0	0.57	172	NE	NE	NE
				PRIMARY PAPER SLUDGE R				
42	WpR2	2.7	83.6	0.47	205	NE	NE	NE
43	WpR3b	1.4	85.7	.55	202	95.1	3.6	29.2
44	WpR3b	1.4	85.4	.48	203	NE	NE	NE
				PRIMARY-SECONDARY PAPER SLUDGE B				
45	WpBs1d	1.0	85.3	0.53	204	94.0	3.1	26.8
46	WpBs2	2.1	82.4	.51	216	96.0	1.8	NE
				PRIMARY PAPER SLUDGE C				
50	WpC1d	1.0	71.9	0.36	268	NE	NE	NE
51	WpC1	.8	80.2	.46	232	NE	NE	33.5
52	WpC1	1.9	89.6	.57	183	96.7	2.8	33.5
55	WpC1	1.2	84.0	.50	211	NE	NE	NE
56	WpC1	1.9	82.0	.45	218	NE	NE	NE
				PRIMARY PAPER SLUDGE C (ROD MILL GROUND)				
59	WpC1r	0.7	85.2	0.53	206	NE	NE	NE
60	WpC1r	1.4	88.2	.56	191	NE	NE	NE
				PRIMARY PAPER SLUDGE S				
61	WpS1b	1.7	90.5	0.63	178	94.3	4.4	NE
				PRIMARY-SECONDARY PAPER SLUDGE S				
62	WpSs1	1.3	90.3	0.62	179	95.9	3.9	NE
63	WpSs1-5	1.3	82.1	.49	220	NE	NE	NE
64	WpSs1b	1.3	87.5	.55	192	NE	NE	NE

NE Not evaluated.
R-3 Reduction after 3 h.
R_{40} Reduction rate at 40 pct reduction.
RDI Reduction disintegration index.
t_{90} Time to reach 90 pct reduction.
[1]See table 1 for explanation of codes.
[2]Distribution of particles produced during RDI test.

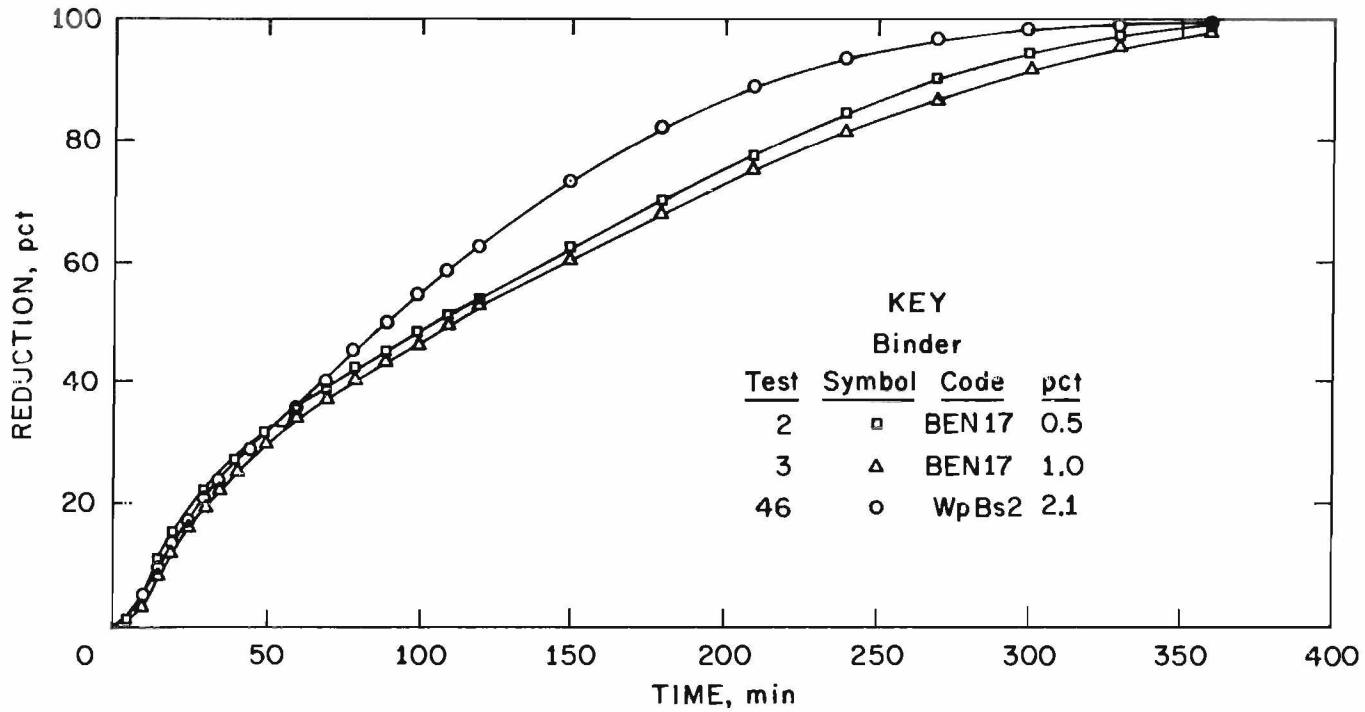

Figure 5.–Reduction kinetics of pellets made with sludge B and bentonite.

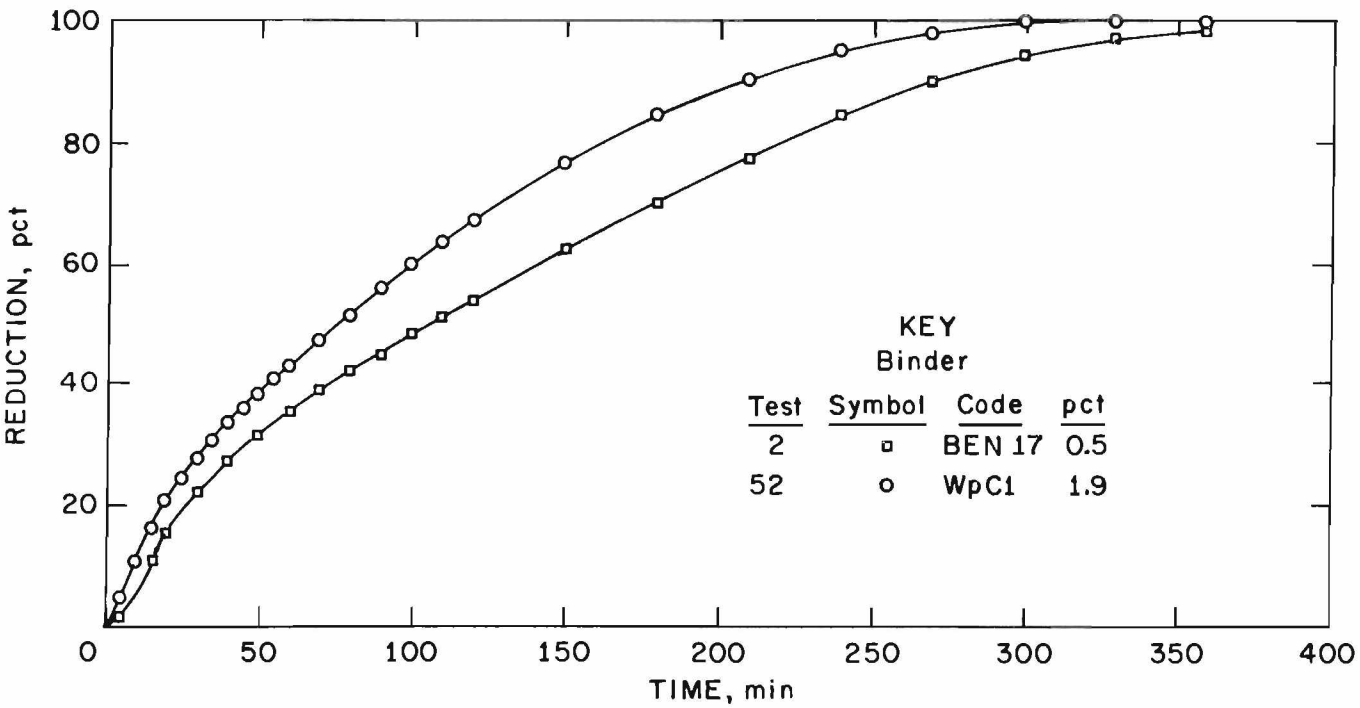

Figure 6.–Reduction kinetics of pellets made with sludge C and bentonite.

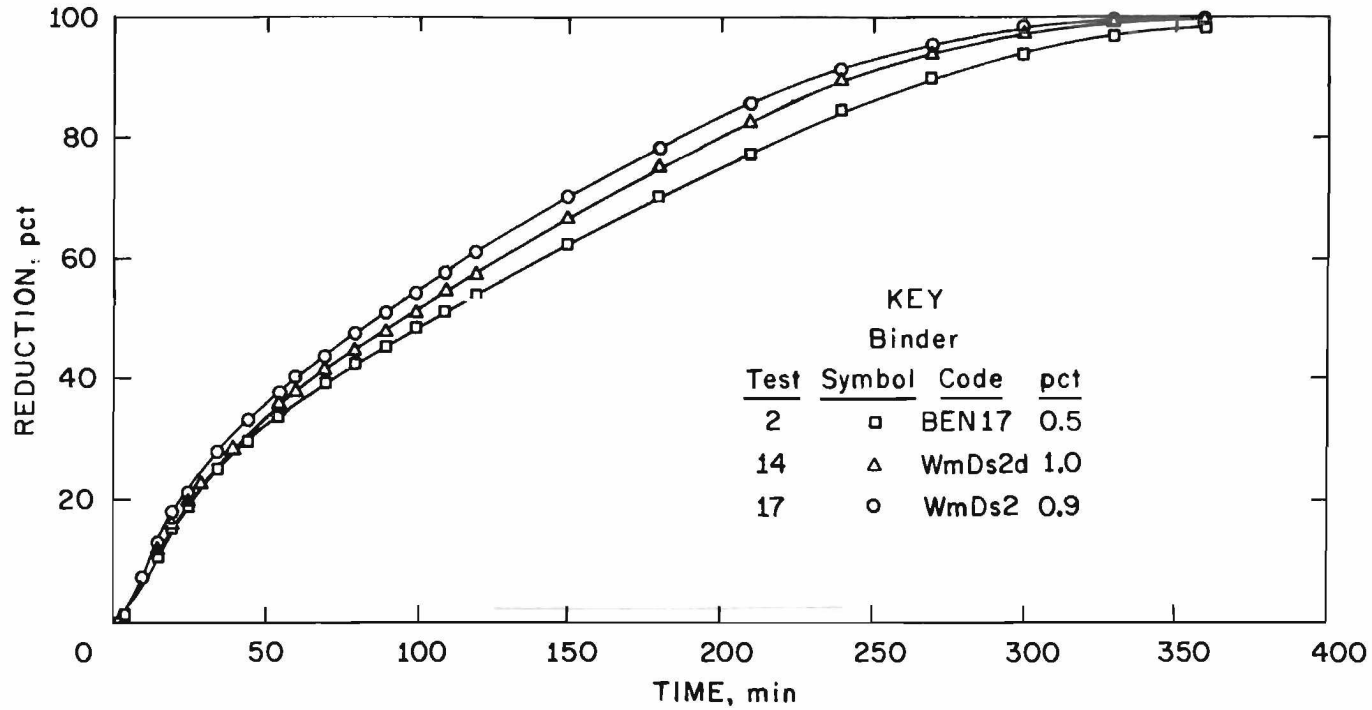

Figure 7.–Reduction kinetics of pellets made with sludge D and bentonite.

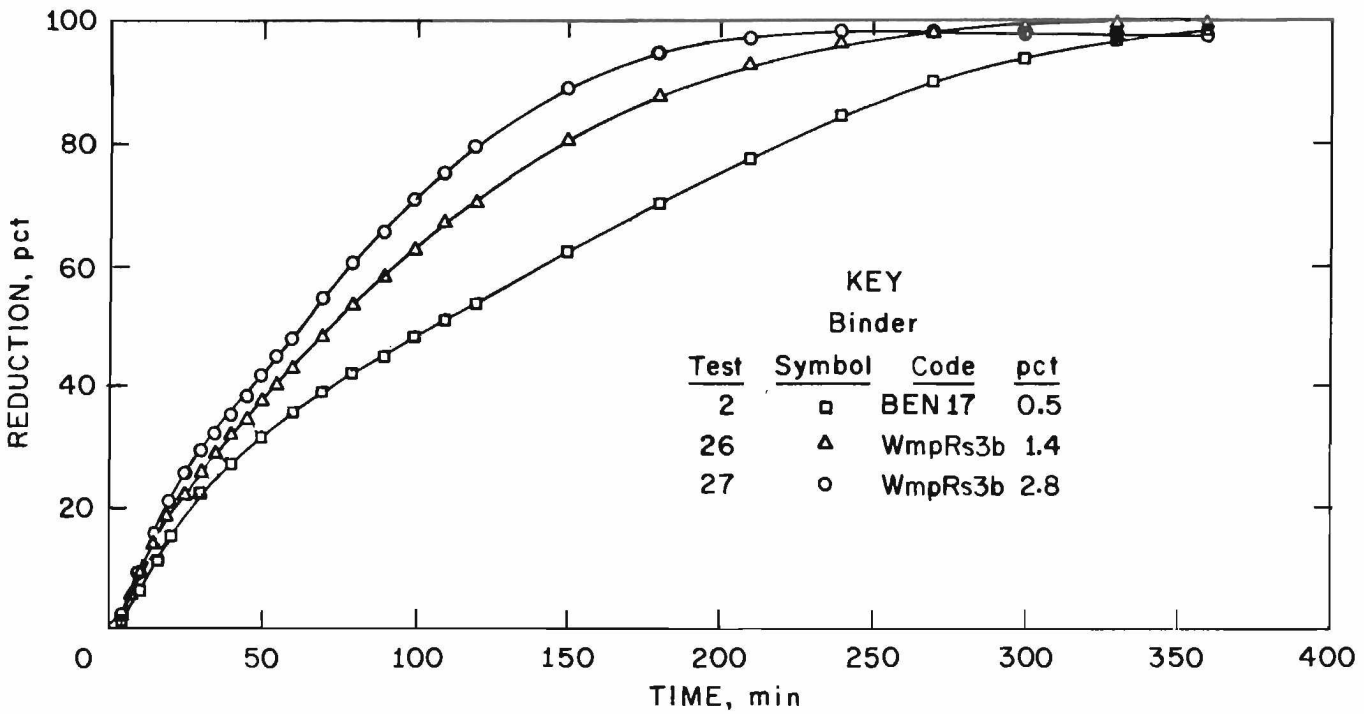

Figure 8.–Reduction kinetics of pellets made with sludge R and bentonite.

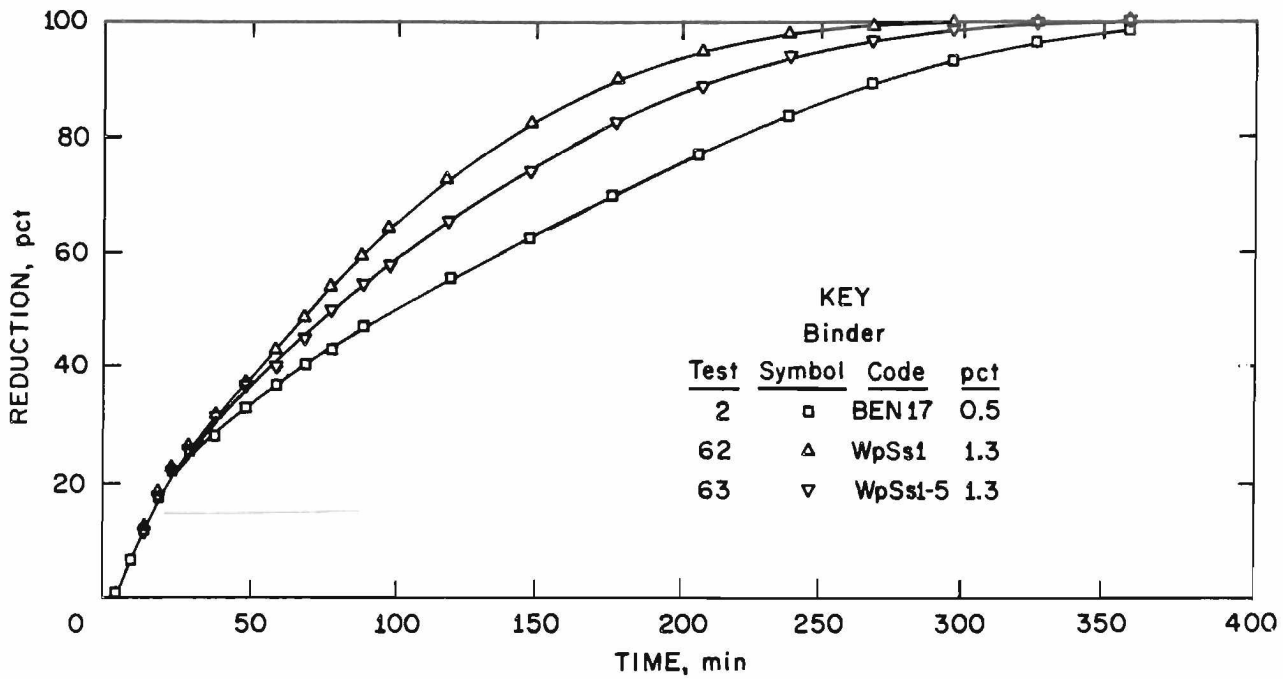

Figure 9.–Reduction kinetics of pellets made with sludge S and bentonite.

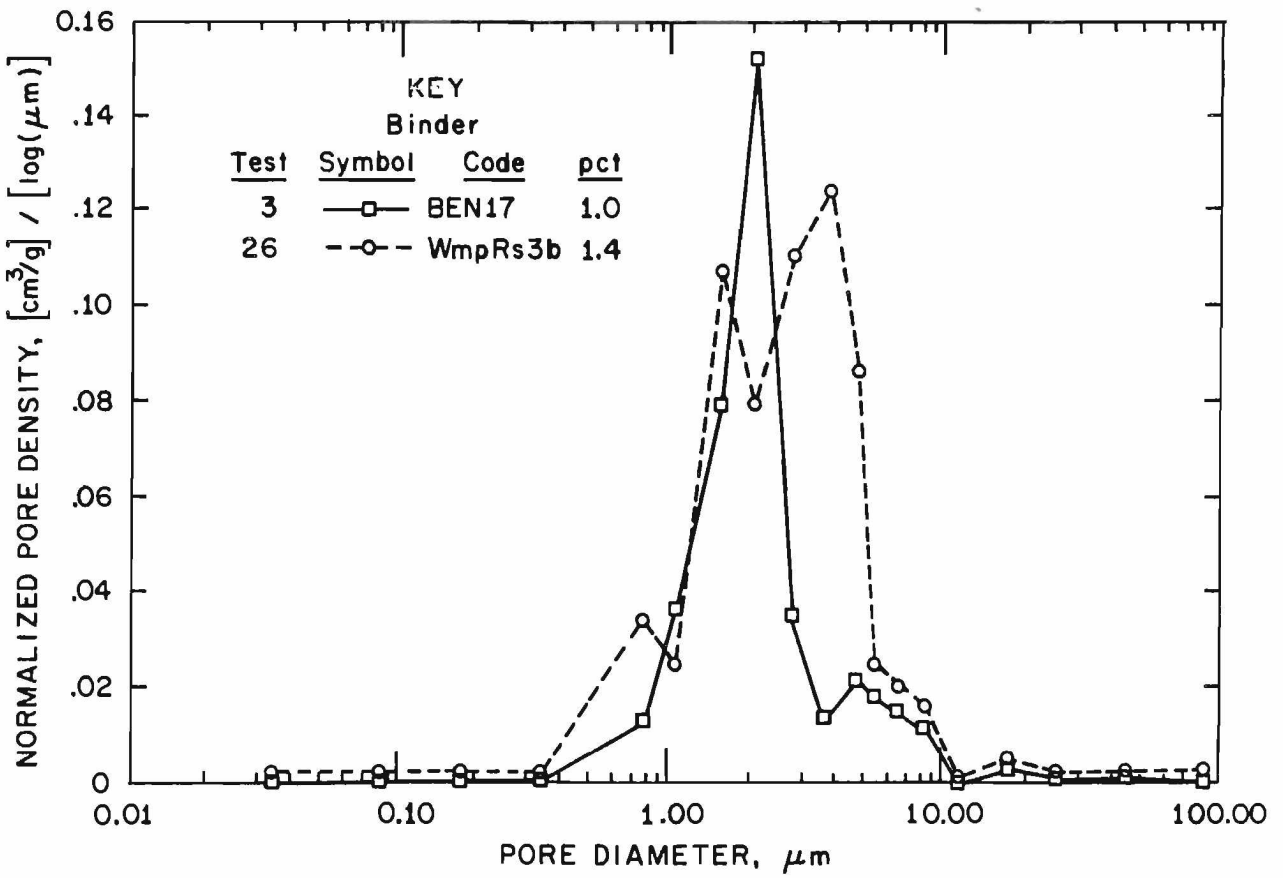

Figure 10.–Pore size and density distribution of pellets made with bentonite and R sludge binders.

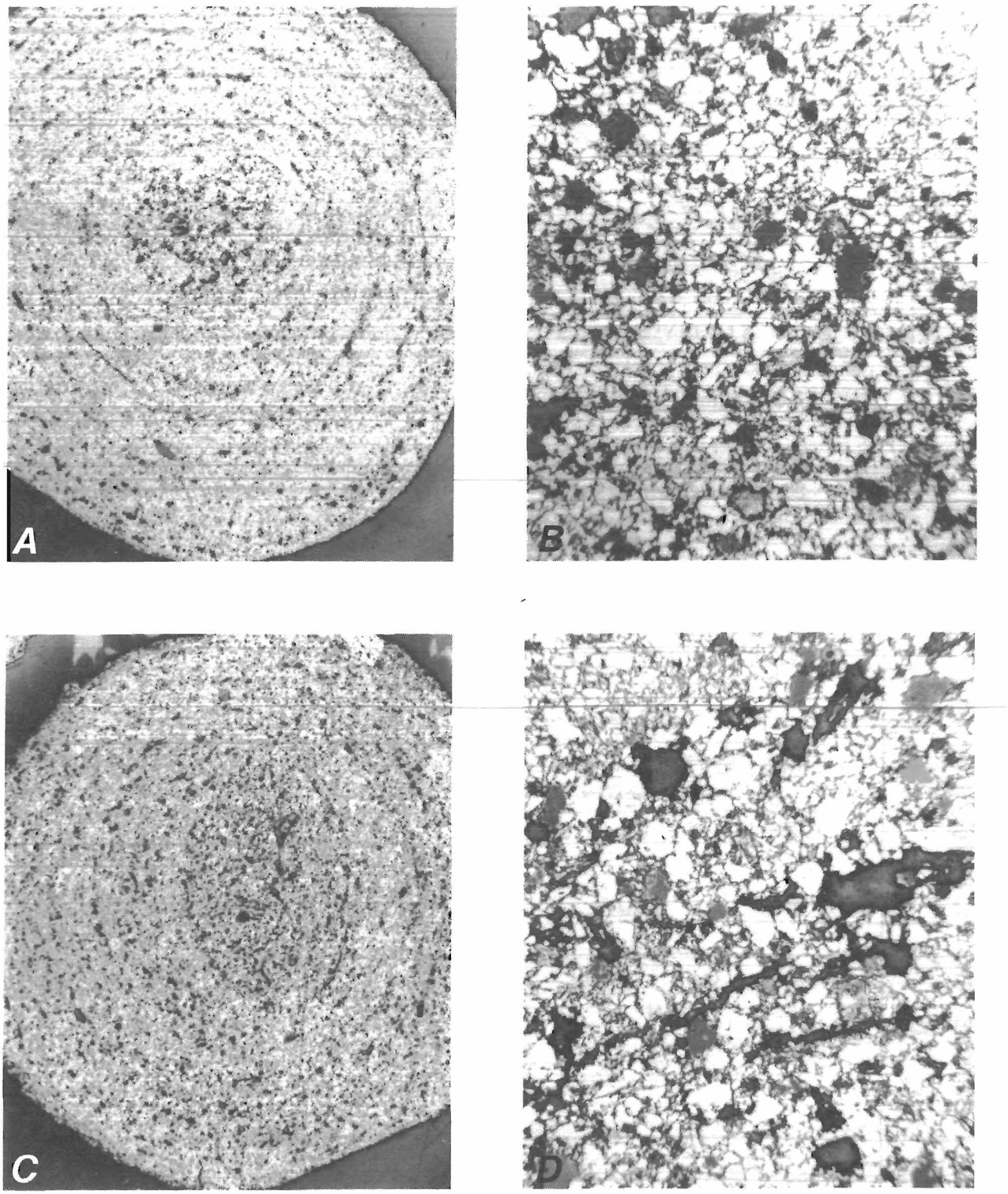

Figure 11.–Photomicrographs of pellets made from bentonite (*A*, X 8; *B*, X 128) and WmDs1 sludge (*C*, X 8; *D*, X 128).

Table 8.–Partial[1] chemical analyses of fired pellets with various levels of binder additions

Binder[2]	Addition	[3]Fe	Si	Al	Ca	Mg
BEN17	0.5	64.7	2.7	0.20	0.30	0.27
	1.0	64.7	2.9	.26	.31	.30
WmDs2d	1.0	64.2	2.6	<.20	<.30	.30
	2.0	64.1	2.6	<.20	<.30	.31
WmpRs1d	1.0	64.8	2.6	<.20	.30	.28
	2.0	64.8	2.7	<.20	.30	.29
WmpRs3d	1.4	64.7	2.7	.20	.31	.27
	2.8	64.4	2.7	.23	.32	.31
WpBs2	2.1	64.1	2.8	.35	.32	.28
	2.9	64.1	2.8	.38	.35	.28
WpC1d	1.0	64.9	2.6	.20	.35	.28
	1.9	64.6	2.6	.24	.36	.28
WpSs1	1.3	64.2	2.7	.22	<.30	.27
	1.7	64.3	2.7	.26	<.30	.27

[1]Other elements: K and Na, <0.05 pct; Ti, <0.3 pct; P, <0.02 pct.
[2]See table 1 for explanation of codes.
[3]Ferrous concentration was <0.1 pct with all pellets except with 1 pct BEN17 binder (0.7 pct).

Low-Temperature Reduction Disintegration

The target value for the low-temperature reduction disintegration index (RDI) was arbitrarily defined as >92 pct for the plus 6.3-mm size and <5 pct for the minus 0.5-mm size. Pellets made with sludge binders disintegrated slightly more than those made with bentonite. When the sludge addition was too high (about 2 pct dry equivalent weight), the target RDI and FCS values were not obtained (tables 6 and 7, test 27). These results suggest that an optimum sludge addition level is needed to obtain the target values.

High-Temperature Softening-Melting

The softening-melting tests were conducted with pellets made with 1 pct bentonite (table 7, test 3), and 1.4 pct (dry equivalent) sludge R (test 26). Sludge R was chosen because it contained all three sludge classes and all the target values were met with the nonagitated mixing method. The results shown in figure 12 indicate that the 10 mm Hg pellet bed pressure drop (softening temperature) occurred more than 150° C higher with sludge binder than with bentonite. Also, the pellet bed shrinkage in the temperature range of 1,250° to 1,450° C was lower with the sludge binder. The pellet melting temperatures (temperatures at which shrinkage rapidly goes to 100 pct) were about the same with the two binders. The chemical analysis of both collected melts after the test were >95 pct Fe; 2 pct C; <0.1 pct Si, Mg, Ca, or P; and <0.02 pct S.

The higher softening temperature and lower shrinkage for pellets made with sludge R should make these pellets a better blast furnace charge material (*3-4*). However, large-scale testing would be required to confirm these preliminary findings.

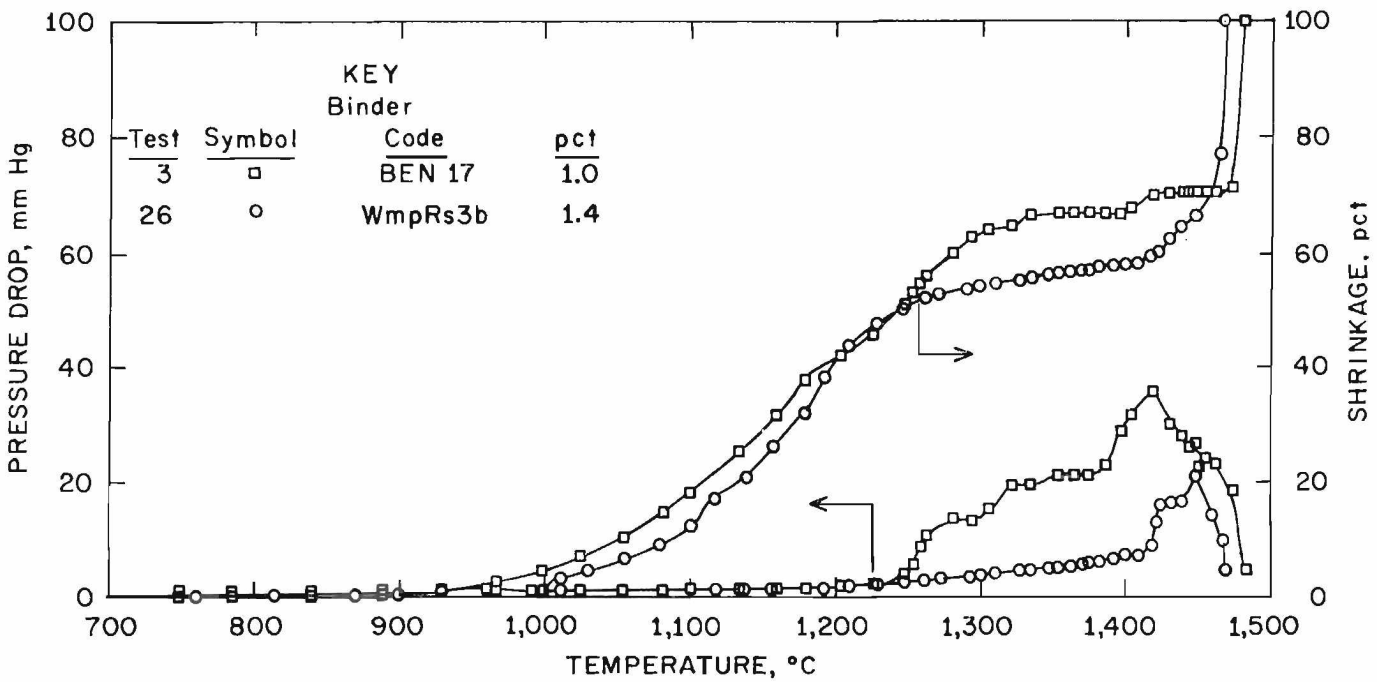

Figure 12.–Temperature dependence of pressure drop and shrinkage for pellets made with sludge R and bentonite binder.

Pellet and Sludge Leaching

Sludges may contain toxic components that may be transferred to surface water runoff from pellet storage piles. Cursory leaching experiments were conducted on raw sludge and pellets made with a sludge binder. In the first experiment, a 1-kg batch of indurated pellets, made with 5 pct raw WmpRs3b sludge binder, was soaked in 0.8 L of distilled and deionized water at ambient conditions in a covered container. For comparison, an equivalent amount (50 g) of the same sludge was soaked under the same conditions in another container. After 1 month, a 0.1-L aliquot was withdrawn from the supernatant liquid in each container. The ions of Ba, Cd, Cr, Cu, Fe, Hg, and Ni could not be detected (<0.2 ppm) in the sludge pellet leach solution. The Mn and Zn contents in the pellet leach solution were also <0.2 ppm. However, in the sludge leach solution, they were 3.1 and 0.3 ppm, respectively. The total dissolved solids (TDS) were 260 and 470 ppm in the pellet and raw sludge leach solutions, respectively.

A larger scale experiment was conducted with 15 kg of indurated pellets made with 5 pct raw WpCl sludge binder and 0.5 kg of this raw sludge, each soaked separately in 50 L of distilled and deionized water. After 1 month, the leach solutions were removed and 99 pct of the water was boiled off in order to concentrate the liquids. The liquids were analyzed and essentially the same results were obtained as with the raw sludge R and pellets in the small-scale leach experiment. The individual calculated concentrations of Ba, Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn from the pellet leach solution were less than 5 ppb. The concentration of Cd, Cr, Hg, Ni, and Zn in the sludge leach solution were the same as with the pellet leach solution, however, some metal concentrations were higher. For example, the sludge leach solution contained 350 ppb Ba, 7 ppb Cu, 9 ppb Mn, and 6 ppb Pb. The TDS values were 12 and 355 ppm for the pellet and sludge leach solutions, respectively. The leaching results suggest that the concentration of the detectable metals were generally higher in the raw sludge leaching solution than in the pellet solution.

SUMMARY AND CONCLUSIONS

Pulpmill and papermill sludges, obtained from five different sources, were evaluated as potential binders for an iron ore concentrate. These waste samples were classified as primary paper sludge, primary-secondary paper sludge mixtures with and without municipal sewage wastes, and secondary paper-municipal sewage sludge. The secondary paper-municipal sewage sludge D contained the lowest quantity (1 pct) of coarse fibers, the highest colloid (47 pct) content, and the most alkali compounds. The primary and primary-secondary paper sludges had higher coarse fiber contents and were more difficult to mix with the taconite concentrate.

With the nonagitated kitchen-type or muller mixing methods, the target physical and metallurgical values were met with four out of the five raw sludges at the 5-pct wet (about 1-2 pct dry equivalent) addition level. The fifth sludge binder (C) contained the highest quantity of coarse fibers (50 pct), and produced pellets with low fired compressive strengths and some surface spalling. When this sludge was agitated (reslurried) at 2 pct solids, mixed with the wet concentrate, filtered, and the filter cake pelletized, no sludge clumps were visible in the filter cake or in the broken pellets. With this reslurried sludge method, all the target values with sludge C were met; however, the filtration time was about three times longer than when filtering concentrate alone.

Drying and grinding the raw sludges aided mixing but decreased the sludge binding efficiency. This behavior was possibly due to the lower degree of hydration of the dried sludges. Wet grinding the sludge did not decrease the binding efficiency, but the addition of this ground sludge to the concentrate slurry tripled the filtration time as compared to filtering the concentrate alone.

The green pellet physical properties (drop number and dry compressive strength) and reducibility of fired pellets increased with increasing sludge additions. However, at levels above about 2 pct dry equivalent weight addition, only a small increase was obtained in the dry compressive strength, and the fired strength and reduction disintegration target values could not be obtained.

To obtain the target pellet physical properties, the dry equivalent weight addition level with raw sludge binder had to be about twice as much as with bentonite and about 10 times more than with pure organic gelled polymers. However, the metallurgical properties of the pellets made with raw sludge binders were superior to those made with bentonite binder. For example, the pellet reducibilities were over 30 pct higher with all the raw sludge binders than with bentonite. Sludge D had the lowest reducibility enhancement. It contained the lowest fiber and the highest alkali metal contents. The pellet softening temperature was over 150° C higher with sludge R binder. Even though more raw sludge than bentonite was required, the sludges have virtually no value, and could be cost effective for producing superior pellets. Large-scale testing would be required to confirm these laboratory results.

REFERENCES

1. Schottman, F. J. Iron Ore. Sec. in BuMines Mineral Commodity Summaries. 1988, p. 78.

2. Skillings, D. N., Jr. U.S. Iron Ore Industry To Recover Moderately in 1987 to Level of 45 Million Gross Tons of Pellets and Ore. Skillings' Min. Rev., v. 76, No. 30, July 25, 1987, pp. 14-23.

3. Anderson, R. C., and D. G. Bonamer. An Improved Acid Pellet From Eveleth Mines. Paper in Proceedings of 60th Annual Meeting of MN Section of AIME, (Univ. MN, Duluth, MN, Jan. 14-15, 1987). Univ. MN, 1987, pp. 3-1–3-26.

4. De Souza, R. P., C. F. Mendonca, and T. Kater. Production of Acid Iron Ore Pellets for Direct Reduction Using an Organic Binder. Min. Eng. (Littleton, CO), v. 10, No. 36, 1984, pp. 1437-1441.

5. Das Gupta, R., R. W. Heins, T. D. Tiemann, and J. A. Clum. Additives To Increase Bentonite Effectiveness in Iron Ore Pelletizing. Soc. Min. Eng. AIME preprint 78-B-97, 1978, 8 pp.

6. Clum, J. A. Substitutes for Western Bentonite in Magnetic Taconite Pellets. Soc. Min. Eng. AIME preprint 76-B-11, 1976, 29 pp.

7. Fine, M. M., and W. C. Wahl. Iron Ore Pellet Binders From Lignite Deposits. BuMines RI 6564, 1964, 18 pp.

8. Goksel, M. A. Organic Binders and Their Behaviors in Iron Ore Pellets During Firing. Paper in Proceedings of the 19th Biennial Conference of the Institute of Briquetting and Agglomeration (Baltimore, MD, Sept. 17-19, 1985). IBA, Erie, PA, 1986, p. 22.

9. Haas, L. A., J. A. Aldinger, and R. K. Zahl. Effectiveness of Organic Binders for Iron Ore Pelletization. BuMines RI 9230, 1989, 21 pp.

10. Humphrey, C. W. Method of Producing Strong Fired Compacts From Iron or Iron Oxide Containing Materials. U.S. Pat. 3,567,811, Mar. 2, 1971.

11. Kuriakose, A. K., D. H. H. Quon, K. E. Bell, and J. A. Soles. Extrusion and Induration of Iron Ore Using Polymers and Calcium Carbonate as Plasticizer/Bond. Paper in Process Mineralogy VI, ed. by R. D. Hagni (Proc. Annu. AIME Meet., New Orleans, LA, Mar. 2-6, 1986), Metall. Soc. AIME, 1986, pp. 485-498.

12. Kramer, W. E., W. J. Ward, and R. W. Young. Pelletizing Iron Ore With Organic Additives. Paper in Proceedings of 29th Annual Mining Symposium (Univ. MN, Duluth, MN, Jan. 15-17, 1968). Univ. MN, 1968, pp. 145-151.

13. Nigro, J. C., and C. Prasky. High Strength Iron Oxide Pellets by Polymer Impregnation. Paper in Proceedings of 12 Biennial IBA Conference of the Institute of Briquetting and Agglomeration (Vancouver, British Columbia, Canada, Aug. 1971). IBA, Erie, PA, 1971, pp. 125-144.

14. Roorda, H. J., and M. J. Jipping. Process for Producing Agglomerates of Metal Containing Ores and the Product of the Process. U.S. Pat. 4,288,245, Sept. 8, 1981.

15. Roorda, H. J., O. Burghardt, H. A. Kortmann, and T. Kater. Production of Fluxed Iron-Ore Pellets for Direct Reduction Using Cellulose Binders. Paper in Proceedings of the 3d International Symposium on Agglomeration (Nuremberg, Federal Republic of Germany, May 6-8, 1981). AIME, pp. B152-B164.

16. Sastry, K. V. S., A. Negm, and T. Kater. Role of Binders During Pelletization of Iron Ore Concentrates–Pellet Growth and Strength Aspects. Paper in Proceedings of the 4th International Symposium on Agglomeration (Toronto, Ontario, Canada, June 2-5, 1985). Soc. Min. Eng. AIME, 1985, pp. 41-48.

17. Shusterich, F. L. Production of Peridur Pellets at Minorca. Skillings' Min. Rev., v. 74, July 13, 1985, pp. 6-10.

18. Steeghs, H. R. G., and T. Kater. Recent Experience With Organic Binders for Iron Ore Pelletizing. Skillings' Min. Rev., v. 73, Dec. 15, 1984, pp. 6-11.

19. Panigraby, S. C., and M. Rigaud. Substitution of Bentonite With Peat Moss and Its Effect on Pellet Properties. Paper in Proceedings of 4th International Symposium on Agglomeration (Toronto, Ontario, Canada, June 2-5, 1985). Soc. Min. Eng. AIME, 1985, pp. 75-82.

20. Wakeman, J. S., E. C. Bogren, and D. J. Kawulok-Englund. A Review of Bentonite Test Methods Being Developed by the Iron Ore Industry. Paper in Proceedings of 3d International Symposium on Agglomeration (Nuremberg, Federal Republic of Germany, May 6-8, 1981). AIME 1981, pp. B120-B132.

21. Blosser, R. O., and R. A. Miner. Sludge Handling and Disposal Practices in the U.S. Pulp and Paper Industry. Pres. at 90's EUCEPA Symposium (Helsinki, May 19-22, 1986); available from NCASI, 260 Madison Ave., New York, 12 pp.

22. Dickinson, S. K. Use of Papermill/Sewage Sludge and Composted Sludge in Mineland Revegetation. Pres. at 1986 National Meeting of ASSMR (Jackson, MS, Mar. 17-20, 1986); available from S. K. Dickinson, IRRRB, Calumet, MN, 4 pp.

23. Luonsi, A., P. Vuoriranta, and P. Hynninen. Reduction of Pulp and Paper Industry Effluent Loading. Water Sci. and Technol., v. 18, 1986, pp. 109-125.

24. Miner, R. A. A Review of Sludge Burning Practices in Combination Fuel-Fired Boilers. NCASI Air and Stream Improvement, Inc., Tech. Bull. 360, Nov. 1981, 27 pp.

25. Eck, T. H. Primary and Secondary Sludge Disposal by Spray Irrigation. Tappi J., v. 69, No. 11, 1986, pp. 54-59.

26. Onoda, G. Y., and L. L. Hench (eds.). Ceramic Processing Before Firing. Wiley, 1978, pp. 235-251.

27. Genco, J. M., and J. J. Carbonello. Dewatering Secondary Sludge–A Pilot-Plant Study. Tappi J., v. 63, No. 6, 1980, pp. 99-102.

28. Reinhardt, J. J., and D. F. Kolberg. Tough Environmental Requirements Demand New Approaches to Landfill. Pulp and Paper, v. 52, Oct. 1978, pp. 128-133.

29. Haas, L. A., J. A. Aldinger, R. L. Blake, and S. A. Swan. Sampling, Characterization, and Evaluation of Midwest Clays for Iron Ore Pellet Bonding. BuMines RI 9116, 1987, 44 pp.

30. American Society for Testing and Materials. Standard Test Method for Water Absorption of Bentonite–Porous Plate Method. E946-83 in 1984 Annual Book of ASTM Standards: Volume 03.05, Section 3, Chemical Analysis of Metals and Metal-Bearing Ores. Philadelphia, PA, 1984, pp. 894-896.

31. Haas, L. A., J. C. Nigro, and R. K. Zahl. Utilization of Simulated Coal Gases for Reducing Iron Oxide Pellets. BuMines RI 8997, 1985, 14 pp.

32. International Organization for Standardization. Iron Ores–Determination of Relative Reducibility. ISO/DIS 7215, 1983, 8 pp.

33. _____. Iron Ores–Low-Temperature Disintegration Test–Method Using Cold Tumbling After Static Reduction. ISO 4696, 1984, 7 pp.

34. Anderson, R. C., D. G. Bonamer, D. A. Painter, and R. W. Rankin. An Improved Acid Pellet From Eveleth Mines and Its Performance at Rouge Steel Co. Skillings' Min. Rev., v. 76, Aug. 15, 1987, pp. 6-9.

APPENDIX.–SLUDGE BACKGROUND

SOURCES

The main emphasis of this report is on the utilization of pulpmill and papermill sludges as an iron oxide binder, but since some of these sludges also contain municipal sewage wastes, that material is also included. On a dry-weight equivalent basis, the U.S. pulp and paper industry generates over 2 million st of sludge per year (*21*).[1] Minnesota has over 13 million acres of forest and has at least six pulpmills and papermills located within 200 miles of the Mesabi Iron Range. These paper operations produce over a million short tons of paper products per year and one plant is known to landfill about 12,000 dry st of sludge per year (*22*). It has been reported (*23*) that the portion of waste sludge per ton of paper produced is about 6 pct for a papermaking operation using the sulfite processing method. The results from various types of paper production operations were tabulated (*21*) and it was reported that the sludge generation rates varied from 0 to 20 pct of the amount of paper produced, with the highest rates occurring during the production of nonintegrated tissue from wastepaper. Processing-waste sludges result from various operations such as pulp rejects (coarse fibers), spillings, and dumping of mixes that do not meet papermaking specifications. In general, the ingredients in the sludges are some of the same materials that are used in papermaking (*23*).

TYPES

The three main classes of processing sludge wastes discussed in this report are primary, secondary, and municipal. The primary and secondary sludges are the material that settle out of the primary and secondary paper treatment clarifiers, respectively. The primary sludges are usually fibrous while the secondary sludges are usually more like mud. The U.S. production rate of primary sludge is about seven times greater than that of secondary sludge (*21*). The mudlike properties of the secondary sludges are probably due to the presence of clay, gelled organic polymers, and bacterial mass. The secondary sludge treatment process normally involves biological action and, in the case of wastewater treatment, is sometimes referred to as the activated biological sludge process.

INGREDIENTS

The content of sludges varies depending on the type of pulpmill and papermaking operation and the relative ratios of pulp, paper, and municipal sewage waste. Some sludge treatment operations only receive waste slurries from a pulpmill, while others may also receive sludge from a papermaking operation. In some incidents, these operations are located close to a municipality, and then both pulp-paper processing and municipal sewage wastes have been combined. The municipal sludges generally contain more nitrogen, phosphorous, and potash and are more useful as a fertilizer. Municipal sludge usually has a soft, wet consistency that is similar to the secondary papermaking sludge. Primary sludge is more fibrous and contains more wood materials that were not completely converted into fine cellulose fibers during the wood pulping process or were lost from the papermaking process.

Different methods are used for separating the natural adhesives found in wood from the cellulose fibers. The wood pulping methods generally can be divided into three categories: mechanical, semichemical, and chemical. Chemical pulping involves cooking the wood at elevated temperatures and pressures in sulfur-containing solutions. The most common chemical pulping method is the Kraft process. The semichemical pulping method uses partial chemical pulping to prepare the wood for subsequent mechanical processing. Mechanical wood pulping relies primarily upon mechanical action to separate the fibers.

INORGANIC CONTENT

In addition to the influence of the wood pulping operation on the chemical content of the sludge, the additives used during the papermaking process also contribute to the sludge composition. The inorganic additives can make up 70 to 90 pct of the dry solids added in a paper-coating process. Some of the common additives are fillers, such as clays, while other additives, like titanium dioxide and calcium carbonate, are used for the control of sheet opacity. Kaolin and China clays are the main filler additives. A survey of 53 papermills showed that the titanium content in the sludge ash varied from 0.3 to 7.6 pct (*24*). A large quantity of calcium carbonate is used in book and cigarette paper production, but it is also used for pH adjustment in most operations. Paper sludge ash may contain up to 21 pct Ca and 2 pct Mg, but municipal sludge may have higher (25 pct) Ca contents (*24*). Municipal sludge can contain up to 10 pct Cr, while paper waste sludge may only contain up to 0.2 pct Cr (*24*), but normally contains less than 0.01 pct. The calcium, magnesium, and titanium compounds may be favorable constituents in the sludge when it is used as a pellet binder because their oxides have high melting points.

ORGANIC CONTENT

In the papermaking processes, various organic polymers are used as additives to improve the wet and dry paper properties, and serve as deflocculants, defoamers, and dyes. Large quantities of starches are used for enhancing fiber-to-fiber bonding. Other added adhesives are guar

[1]Italic numbers in parentheses refer to items in the list of references preceding this appendix.

gums, polyvinyl alcohol, polyvinyl acetate, polyacrylamides, soy protein, and modified cellulose (such as carboxymethyl and hydroxyethyl derivatives). Some of these compounds also aid the paper-sizing operation, making the sheets more resistant to the penetration of liquids.

The chain length and composition of some of the organic adhesives change during the paper waste processing operation. Treatment processes, such as aerobic or anaerobic digestion, and heat treatment, decrease the volatile solids content of the sludge. Lime treatment can improve the sludge dewaterability. In the clarification and densification treatment process, large quantities of organic flocculants and ferric and aluminum compounds may be added. For example, one 450-st/d newsprint operation generated 90 dry equivalent st/d sludge (26 pct solids) and used approximately 1,600 lb/d organic polymer and 3,000 lb/d alum (*25*).

USES

Sludges have been used as fertilizers, soil conditioners, animal feed, and fuel. Presently most of the sludge is disposed in landfills. A survey (*21*) conducted in 1979 showed that the sludge distribution was 86 pct to landfills, 11 pct to incineration plants, and the remaining 3 pct to agricultural and other uses. The recent trend has been to dispose of more sludge by incineration. Construction of an incinerator is expensive; however, if the sludge could be added to iron oxide pellets, combustion and firing equipment may be already available.

COSTS

The economic viability of processing schemes must be viewed not as a profit potential but rather in terms of the cost relative to incineration, on-land disposal, or other options. Chemical conditioning of biological (secondary) sludges has been reported to cost up to $50/st (*21*). The operating cost of flash drying a low-ash sludge, containing between 33 and 54 pct solids prior to incineration, was reported as $21/dry st (*24*). The cost for land disposal for 11 mills varied between $18/dry st and $144/dry st (*24*). The transportation distance and the percent solids are the major variables in determining the sludge disposal cost. In one agricultural use, the sludge (5 pct solids) was hauled by tank truck 20 miles.

PERCENT SOLIDS

At the present time, utilization schemes suffer from the low bulk density and low percent solids of the sludge. On-land disposal methods require a large space near the production site, where space is usually limited because of commercial and residential requirements. The landfilling space requirements for all Wisconsin paper sludges have been estimated as over 1 million yd^3/yr.

Some low-ash (<30 pct) and high-fiber (>20 pct) sludges appear dry and stable at 30 pct solids, while sludges from paper recycling or deinking operations at the same percent solids level appear like a thick fluid. The percent dry solids of sludge can vary from approximately 2 to 50 pct depending on the type of sludge and the dewatering method used.

Sludges are usually dewatered in settling basins or by mechanical equipment. Settling basins are seldom used to dewater secondary sludges. About one-third of the primary sludges are dewatered and partially dried by this method (*21*). Generally the high percent solid sludges are produced with mechanical equipment such as filter presses, vacuum filters, and centrifuges. Belt filter presses are capable of dewatering secondary sludges to between 10 and 20 pct solids (*21*). V-presses have been used to dewater primary sludges with high fiber contents to levels between 30 to 40 pct solids (*21, 23*). Recently an improved screw press was installed with a high-pressure zone that consistently produced sludge with 45 to 50 pct solids. Steam injection into some presses has increased the sludge solids content by 5 pct. To improve the dewatering of secondary sludge, primary sludge is sometimes added so it can be dewatered with presses. Approximately one-third of the papermills are combining the secondary sludges with primary sludges and dewatering them on vacuum filters. Approximately 10 pct of the mills are dewatering the combined sludges using centrifuges (*21*).

Depending on the sludge use, further drying may be required. Milorganite (produced in Milwaukee, WI, from municipal sewage waste) is used for fertilizer. Its moisture content is decreased from 86 to about 5 pct in a large rotary drum dryer at 650° C, at a rate of about 1,000 st wet filter cake per hour. Some sludges are air dried in windrows such as composting operations. Aeration of the windrows enhances the bacterial reactions and more heat is generated. A recent research paper reported that composting of paper sludge can produce temperatures of over 55° C in northern Minnesota when the ambient temperature was between -17° and -25° C, but initially air had to be blown through the compost pile (*22*).

DEGRADATION

Carbohydrate-derivative materials (starches, guar gums, and cellulose compounds) are susceptible to degradation by enzymatic attack as a result of the presence of bacteria or fungi. Natural gums are particularly susceptible to degradation. In contrast, organic materials such as polyvinyl alcohol and acrylics, which are not derived from carbohydrates, are less susceptible to biodegradation (*26*). Biodegradation decreases the polymer molecular weight, which results in lower water absorption capacity and adhesive strengths. Degradation can be inhibited by the addition of a preservative or biocide. Microbial activity is likely to be nil when the sludge is dry.

ASHING

The volatile and ash contents have a significant influence on the economics of sludge incineration. The energy required to dry the sludge is proportional to the percent moisture in the sludge. At 25 pct solids, about 1 million Btu/st of sludge is required to remove the water. Therefore, to burn the sludge, the percent solids should be greater than 35 pct. Some companies have burned sludge with 20 pct solids but in conjunction with drier solids. The mean heat content of sludges being burned is about 8,000 Btu/lb of volatile sludge solids (*21*).

One advantage of high-temperature incineration is that the ash occupies less volume than the raw sludge. In the past, sludges that were burned in incinerators almost invariably contained less than 10 pct ash, but recently some plants have been burning sludges containing over 20 pct ash. Some of the ash content of primary sludge results from the noncombustible paper coating additives, such as kaolin clay. The coatings on the lighter stocks of glossy paper can account for about 30 pct of the total paper weight on a moisture-free basis (*21*).

RAW SLUDGE AND ASH LEACHABILITY

Some sludges and ashes can contain constituents that may get into the ground or surface water if disposed on land. The main constituents of paper sludges are cellulose fibers, clay filler, and lime, but other chemical additives are also used to produce different types of paper products. For example, many deinking operations and some paper-coating operations produce sludges that contain relatively high heavy-metal concentrations as compared to sludge produced by other paper-processing operations but the concentrations generally are lower than municipal sludges. High heavy-metal sludges, or their nonfused ash products, may cause environmental problems if deposited in landfills or used as soil conditioners. In order to prevent the excursion of the water-soluble constituents, many sludge landfills are lined with an impermeable material and the leachate is collected (*21*). Recently there have been concerns on the possible presence of 2,3,7,8-tetrachloro dibenzo-p-dioxin (2,3,7,8-TCDD) in pulpmill and papermill sludges (*21*). Utilization of sludge in making iron ore pellets and steel may encapsulate the noncombustible toxic materials into a molten slag and thereby decrease their environmental impact. However, a thorough study would be required to delineate the environmental impact of pellets made with sludge binders.

ASH THERMAL PROPERTIES

The high-temperature properties of ash are very dependent on its source. The initial deformation, softening, and hemispherical fluid temperatures of ash from paper sludge are about 200° C higher than for coal. The sludge-ash fusion temperatures are about 25° C higher in oxidizing than reducing environments (*24*). These ash melting characteristics may influence the iron ore pellet porosity when sludge binder is used to pelletize iron ore concentrate.

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